165377

DATA VALIDATION PLAN (Volume 2 of 2)

Sauget Area 1
Support Sampling Project

Solutia, Inc.
St. Louis, Missouri

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O'BRIEN & GERE
ENGINEERS, INC.

Section 8

O'Brien & Gere Engineers. Inc. Data Validation Form – USEPA Method 8290 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8290 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS – Partial Validation

SECTION 8

O'Brien & Gere Engineers Data Validation Form

USEPA Method 8290 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS

Date:____________________ Number of samples and compounds per sample:______________

Project Number:____

Validator:____Equipment Blanks:________

Project: ____Blind/Field Duplicates:______

Laboratory:____MS/MSDs:____________

QAPP:__________________________________ DV Guidelines: USEPA Region II

Laboratory package number:_________________FULL VALIDATION

Method reference:

- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846. 3rd Edition. Washington D.C.*

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8290	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8290	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms

Method 8290 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS

The following worksheets are based on:

- USEPA. 1994 *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)*. Albany, New York.
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd Edition. Washington D.C.*

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VALIDATION DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the qualifiers assigned to results in the data validation process.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

U - Not detected above the reported detection limit.

NJ - There is presumptive evidence for the presence of the compound at an estimated value.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

METHOD 8290 INFORMATION

Scope and Application
Method 8290 method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs) and polychlorinated dibenzofurans tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations.

Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs) considered within the scope of this method that are greater than ten times the upper MCLs must be analyzed by a protocol designed for such concentration levels, e.g. Method 8280.

The **calibration range** of the method for a 1 L water sample is 10 to 2000 ppq for TCDD/TCDF and PeCDD/PeCDF, and 1.0 to 200 ppt for a 10 g soil, sediment, fly ash, or tissue sample for the same analytes. Analysis of a one-tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper MCL.

Summary of Method
This procedure uses matrix specific extraction, analyte specific cleanup and HRGC/HRMS analysis techniques.
If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination.

A specified amount is spiked with a solution containing specified amounts of each of the nine isotopically ($^{13}C_{12}$) labeled PCDDs/PCDFs. The sample is then extracted according to a matrix specific extraction procedure. Aqueous samples that are judged to contain 1 percent or more solids, and solid samples that show an aqueous phase, are filtered, the solid phase (including the filter) and the aqueous phase extracted separately, and the extracts combined before extract cleanup. The extraction procedures are:

The extracts are submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the extracts are cleaned up by column chromatography on alumina, silica gel and activated carbon.

The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding 10 to 50 µL (depending on the matrix) of a nonane solution containing 50 pg/µL of the recovery standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners, while the latter is used to determine the percent recoveries of hexa-, hepta-, and octachlorinated PCDD/PCDF congeners.

The µL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

The identification of OCDD and nine of the fifteen 2,3,7,8-substituted congeners for which a 13C-labeled standard is available in the sample fortification and recovery standard solutions, is based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous detection of the two most abundant ions in the molecular ion region.

The remaining six 2,3,7,8-substituted congeners (i.e. 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standards are available in the sample fortification solution, and all other PCDD/PCDF congeners are identified when their relative retention times fall within their respective PCDD/PCDF retention time windows, as established from the routine calibration data, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Identification also is based on a comparison of the ratios of the integrated ion abundance of the molecular ion specie to their theoretical abundance ratios.

Interferences
Interferents coextracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes and polychlorinated alkyldibenzofurans, that may be found at concentrations several orders of magnitude higher than the analytes of interest.

A high-resolution capillary column (60 m DB-5, J&W Scientific, or equivalent) is used in this method. However, no single column is known to resolve all isomers. The 60 m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity. In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent.

Reagents and Standard Solutions
High-Resolution Concentration Calibration Solutions – Five nonane solutions containing unlabeled (totaling 17) and carbon-labeled

(totaling 11) PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (1.0 pg/µL) and the highest values for the octachlorinated congeners (1000 pg/µL).
GC Column Performance Check Solution – This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The $^{13}C_{12}$-2,3,7,8-TCDD is also present.
Sample Fortification Solution – This nonane solution contains the nine internal standards at the nominal concentrations. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances. (Note $^{13}C_{12}$-OCDF is not present in the solution.)
Recovery Standard Solution – This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at a nominal concentration of 50 pg/µL per compound. 10 to 50 µL of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.
Matrix Spike Fortification Solution – Solution used to prepare the MS and MSD samples. It contains all unlabeled analytes at concentrations corresponding to the HRCC 3.

Procedure

Internal standard addition
Use a portion of 1 g to 1000 g (± 5 percent) of the sample to be analyzed. Different sample sizes are required for different matrices. Transfer the sample portion to a tared flask and determine its weight.
Add an appropriate quantity of the sample fortification mixture to the sample. All samples should be spiked with 100 µL of the sample fortification mixture to give internal standard concentrations.

Mass Spectrometer
The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less. At a minimum, the ions listed in the method 6 for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection of the molecular ions M and M+2 for ^{13}C-HxCDF and ^{13}C-HpCDF rather than M+2 and M+4 (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in the method. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors.

Data Acquisition

The total cycle time for data acquisition must be ≤ 1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

Calibration

Initial Calibration – Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration does not meet the required criteria.
Tune the instrument with PFK.
Inject 2 µL of the GC column performance check solution and acquire SIM mass spectral data.
Analyze a 2 µL portion of each of the five concentration calibration solutions.
The ratio of integrated ion current for the ions must be within the indicated control limits for all unlabeled calibration standards and for carbon-labeled internal and recovery standards.
For each selected ion current profile (SICP) and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Measurement of the S/N is required for any GC peak that has an apparent S/N of less than 5:1.
Calculate the 17 relative response factors (RF) for unlabeled target analytes relative to their appropriate internal standards and the nine RFs for the labeled $^{13}C_{12}$ internal standards relative to the two recovery standards according to the following formulae:

$$RF_n = \frac{A_x \text{ X } Q_{is}}{Q_x \text{ X } A_{is}} \qquad RF_m = \frac{A_{is} \text{ X } Q_{rs}}{Q_{is} \text{ X } A_{rs}}$$

where:

A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDD/PCDFs

A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,

A_{rs} = sum of the integrated ion abundances of the quantitation ions for the labeled recovery standards,

Q_{is} = quantity of the internal standard injected (pg)

Q_{rs} = quantity of the recovery standard injected (pg), and

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the mean RF used will be the same.
NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard.
For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer, the mean RF used for those homologous series will be the mean of the RFs calculated for all individual 2,3,7,8-substituted congeners.

Criteria for Acceptable Calibration
The percent relative standard deviations for the mean response factors (RF_n and RF_m) from the 17 unlabeled standards must not exceed ± 20 percent, and those for the nine labeled reference compounds must not exceed ± 30 percent.
The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.
The ion abundance ratios must be within the specified control limits.

Routine Calibration (Continuing Calibration Check) – Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12-hour shift. Inject 2 µL of the concentration calibration solution HRCC-3 standard.

Criteria for Acceptable Routine Calibration – The following criteria must be met before further analysis is performed.
The measured RFs (RF_n for the unlabeled standards obtained during the routine calibration runs must be within ± 20 percent of the mean values established during the initial calibration.
The measured RFs (RF_m for the labeled standards) obtained during the routine calibration runs must be within ± 30 percent of the mean values established during the initial calibration.
The ion abundance ratios must be within allowable control limits.

If either one of the criteria is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire routine calibration process must be reviewed. It is realized that it may not always be possible to achieve all RF criteria. For example, it has occurred that the RF criteria for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD were not met, however, the RF values for the corresponding unlabeled compounds were routinely within the criteria established in the method. In these cases, 24 of the 26 RF parameters have met the QC criteria, and the data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. Corrective action would be in order, for example, if the compounds for which the RF criteria were not met included both the unlabeled and the corresponding internal standard compounds.

Analysis
Inject a 2 µL aliquot of the extract into the GC.
Acquire SIM data
NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined. Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run.

Identification Criteria
Retention Times

For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes must be within −1 to +3 seconds of the isotopically labeled standard.

For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of six congeners), the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the daily routine calibration results.

For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution.

The ion current responses for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

The ion current responses for both ions used for the labeled standards must reach maximum simultaneously (± 2 seconds).
NOTE: The analyst is required to verify the presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF in the SICPs of the daily performance checks. Should either one compound be missing, the analyst is required to take corrective action as it may indicate a potential problem with the ability to detect all the PCDD/PCDFs.

Ion Abundance Ratios
The integrated ion currents for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned.

Signal-to-Noise Ratio
All ion current intensities must be ≥ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers.

Polychlorinated Diphenyl Ether Interferences
In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected at the same retention time (± 2 seconds) in the corresponding polychlorinated diphenyl ether channel.

Calculations
PCDD or PCDF Compounds

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \; RF_n}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,
A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDD/PCDFs,
A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,
Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,
W = weight, in g, of the sample (solid or organic liquid) or volume in mL of an aqueous sample, and
RF_n = calculated mean relative response factor for the analyte (RFn with n = 1 to 17; Sec 7.7.1.4.5).

Percent recovery of the nine internal standards

$$\text{Internal standard percent recovery} = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times RF_m} \times 100$$

Where:

A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standard,
A_{rs} = sum of the integrated ion abundances of the quantitation ions for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners
Q_{is} = quantity, in pg, of the recovery standard added to the sample before extraction,
Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before

HRGC/HRMS analysis, and

RF_m = calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard. This represents the mean. (RF_m with m = 18 to 26).

If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds exceeds the upper method calibration limits (MCL), the linear range of response versus concentration may have been exceeded, and a second analysis of the sample (using a one tenth aliquot) should be undertaken. The volumes of the internal and recovery standard solutions should remain the same as described for the sample preparation. For the other congeners (including OCDD), however, report the measured concentration and indicate that the value exceeds the MCL.

If a smaller sample size would not be representative of the entire sample, one of the following options is recommended:
Re-extract an additional aliquot of sufficient size to ensure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Prior to GC/MS analysis, dilute the sample so that it has a concentration of internal standard equivalent to that present in the calibration standard. Then, analyze the diluted extract.
Re-extract an additional aliquot of sufficient size to ensure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Immediately following extraction, transfer the sample to a volumetric flask and dilute to known volume. Remove an appropriate aliquot and proceed with cleanup and analysis.
Use the original analysis data to quantitate the internal standard recoveries. Respike the original extract (note that no additional cleanup is necessary) with 100 times the usual quantity of internal standards. Dilute the respiked extract by a factor of 100. Reanalyze the diluted sample using the internal standard recoveries calculated from the initial analysis to correct the results for losses during isolation and cleanup.

The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of FC signals included in the homologous total concentration value must be specified in the report.

Sample Specific Estimated Detection Limit – The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

Samples giving a response for both quantitation ions that is less than 2.5 times the background level.

Use the expression for EDL to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions. of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that peak height.

Use the formula:

$$\text{EDL (specific 2,3,7,8-substituted PCDD/PCDF)} = \frac{2.5 \text{ X } H_x \text{ X } Q_{is}}{H_{is} \text{ X } W \text{ } RF_n}$$

Where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDD/PCDFs.
H_x = sum of the height of the noise level for each quantitation ion for the unlabeled PCDD/PCDFs, measured as shown in Figure 6.
H_{is} = sum of the height of the noise level for each quantitation ion for the labeled internal standard, measured as shown in Figure 6.

Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions.

When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria, calculate the "**Estimated Maximum Possible Concentration**" (EMPC).

The 2,3,7,8-TCDD **toxicity equivalents** (TE) of PCDDs and PCDFs present in the sample are calculated. This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDD and PCDFs and to OCDD and OCDF. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds.

The concentration of 2,3,7,8-TCDD is calculated from the analysis of the sample extract on the 60 m DB-5 fused silica capillary column.

The concentration of the 2,3,7,8-TCDF is obtained from the analysis of the sample extract on the 30 m DB-225 fused silica capillary column. However, the GC/MS conditions must be altered so that: (1) only the first three descriptors (I.e., tetra-, penta-, and hexachlorinated congeners) are used; and (2) the switching time between descriptor 2 (pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}C_{12}$-1,2,3,7,8-PeCDD. The chromatographic separation between the 2,3,7,8-TCDF and its close eluters (2,3,4,7-TCDF and 1,2,3,9-TCDF must be equal or less than 25 percent valley.

For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratio criteria. In addition, the retention time identification criterion applies here for congeners for which a carbon labeled analogue is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT.

Quality Control

System Performance Criteria – The response factors and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hour period during which samples are analyzed. An HRGC/HRMS method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch required more than 12 hours of analyses.

GC Column Performance

The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of ≤ 25 percent. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. The retention times are used to determine the eight homologue retention time windows that are used for qualitative and quantitative purposes. All first eluters of a homologous series should be labeled with the letter F and all last eluters of a homologous series should be labeled with the letter L.

Switching Times – Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60 m DB-5 column.

Mass Spectrometer Performance

The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour period of operation.

Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. An acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

Performance Check Solutions
At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound.

The continuing calibration and the mass resolution check must be performed also at the end of each 12-hour period. Furthermore, an HRGC/HRMS method blank run must be recorded following a calibration run and the first sample run.

Deviations from criteria specified for the GC performance check or for the mass resolution check invalidate all positive sample data collected between analyses of the performance check solution, and the extracts from those positive samples shall be reanalyzed.

If the continuing calibration check performed at the end of a 12 hour period fails by no more than 25 percent RPD for the 17 unlabeled compounds and 35 percent RPD for the 9 labeled reference compounds, use the mean RFs from the two daily routine calibration runs to compute the analyte concentrations, instead of the RFs obtained from the initial calibration. A new initial calibration (new RFs) is required immediately (within two hours) following the analysis of the samples, whenever the RPD from the end-of-shift routine calibration exceeds 25 percent or 35 percent, respectively.

Duplicate Analyses

The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean).

Matrix Spike and Matrix Spike Duplicate

The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

Percent Recovery of the Internal Standards - For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (parts per trillion)

	Water	Soil Sediment Paper Pulp[b]	Fly Ash	Fish Tissue[c]	Human Adipose Tissue	Sludges, Fuel Oil	Still-Bottom
Lower MCL[a]	0.01	1.0	1.0	1.0	1.0	5.0	10
Upper MCL[a]	2	200	200	200	200	1000	2000
Weight (g)	1000	10	10	20	10	2	1
IS Spiking Levels (ppt)	1	100	100	100	100	500	1000
Final Extract Volume (μL)[d]	10-50	10-50	50	10-50	10-50	50	50

a For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, by 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

b Sample dewatered

c One half of the extract from the 20 g sample is used for determination of lipid content.

Composition of the Sample Fortification and Recovery Standard Solutions[a]

Analyte	Sample Fortification Solution Concentration (pg/μL; Solvent: Nonane)	Recovery Standard Solution Concentration (pg/μL; Solvent: Nonane)
$^{13}C_{12}$-2,3,7,8-TCDD	10	--
$^{13}C_{12}$-2,3,7,8-TCDF	10	--
$^{13}C_{12}$-1,2,3,4-TCDD	--	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	10	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	10	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	--	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	25	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	25	--
$^{13}C_{12}$-OCDD	50	--

(a) These solutions should be made freshly every day because of the possibility of adsorptive losses to glassware. If these solutions are to be kept for more than one day, then the sample fortification solution concentrations should be increased ten fold, and the recovery standard solution concentrations should be doubled. Corresponding adjustments of the spiking volumes must then be made.

The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

PCDD	**PCDF**
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF

(*) The 13C-labeled analogue is used as an internal standard.
(+) The 13C-labeled analogue is used as a recovery standard.

Isomers of Chlorinated Dioxins and Furans as a Function of the Number of Chlorine Atoms

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2,3,7,8 Isomers	Number of Furan Isomers	Number of 2,3,7,8 Isomers
1	2	--	4	--
2	10	--	16	--
3	14	--	28	--
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	75	7	135	10

High-Resolution Concentration Calibration Solutions

Compound	Concentration (pg/μL), Nonane)				
HRCC	5	4	3	2	1
Unlabeled Analytes					
2,3,7,8-TCDD	200	50	10	2.5	1
2,3,7,8-TCDF	200	50	10	2.5	1
1,2,3,7,8-PeCDD	500	125	25	6.25	2.5
1,2,3,7,8-PeCDF	500	125	25	6.25	2.5
2,3,4,7,8-PeCDF	500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDD	500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDD	500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDD	500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDF	500	125	25	6.25	2.5
2,3,4,6,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDD	500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDF	500	125	25	6.25	2.5
1,2,3,4,7,8,9-HpCDF	500	125	25	6.25	2.5
OCDD	1,000	250	50	12.5	5
OCDF	1,000	250	50	12.5	5
Internal Standards	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDD	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	125	125	125	125	125
$^{13}C_{12}$-OCDD	250	250	250	250	250
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD[a]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[b]	125	125	125	125	125

(a) Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.
(b) Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF and OCDD internal standards.

PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution and Used for Defining the Homologous GC Retention Time Windows on a 60 m DB-5 Column

No. of Chlorine Atoms	PCDD Positional Isomer		PCDF Positional Isomer	
	First Eluter	Last Eluter	First Eluter	Last Eluter
4[a]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
1,2,4,7,9				
6	1,2,4,6,7,9/	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
1,2,4,6,8,9				
7	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,7,8,9
8	1,2,3,4,6,7,8,9	1,2,3,4,6,7,8,9		

(a) In addition to these two TCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$-2,3,7,8- and 1,2,3,9-TCDD isomers must also be present as a check of column resolution.

Theoretical Ion Abundance Ratios and
Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

(a) Used only for ^{13}C-HxCDF (IS)
(b) Used only for ^{13}C-HpCDF (IS)

2,3,7,8-TCDD Equivalency Factors (TEFs) for the Polychlorinated Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF[a]
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,4,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

(a) Taken from "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxin and –Dibenzofurans (CDDs and CDFs) and 1989 Update", (EPA/625/3-89/016, March 1989).

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDF
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDF
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDF (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	TCDF
	[354.9792]	LOCK	C_9F_{13}	TCDF
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8250	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	423.7767	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7780	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[442.9728]	LOCK	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:

H	=	1.007825	0	=	15.994915
C	=	12.000000	^{35}Cl	=	34.968853
^{13}C	=	13.003355	^{37}Cl	=	36.965903
F	=	18.9984			

S = internal/recovery standard

1.0 DATA COMPLETENESS FOR DIOXIN/DIBENZOFURAN ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of PCDD/PCDF data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, ug/L for waters and ug/kg for soils?

1.4 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.5 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.6 Were raw data to support analyses and QC operations present and complete?

Actions: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.7 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.8 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

Criteria:

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Holding times for PCDD/PCDF:
Aqueous and solid samples – 30 days from collection to extraction, 45 days from extraction to analysis.

The holding times for extraction/preparation presented in Method 8290 are considered to be contractual holding times only. There are no demonstrated maximum holding times associated with the extraction/preparation of PCDDs/PCDFs in aqueous, solid, semi-solid, tissues, and other sample matrices. If samples are stored properly, the holding times for extraction/preparation are up to one year. Sample extracts are to be analyzed within 45 days of preparation.

VALIDATION ACTION:
If holding times for analysis of sample extracts are exceeded, positive results and detection limits are considered to be approximate (UJ, J).

2.2 Summarize below the samples qualified due to holding time excursions.
2.3

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 INSTRUMENT PERFORMANCE (MASS CALIBRATION, GC COLUMN PEFORMANCE CHECK)

Criteria:

Mass calibration

Mass calibration of the MS must be performed prior to analyzing calibration solutions, Blanks, samples, and QC samples. The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. A minimum required resolving power of 10000 is obtained for perfluorokerosene (PFK) ion 380.9760. This is done by first measuring peak width at 5% of the maximum. This should not exceed 100 ppm, i.e., it should not exceed 0.038, for ion 380.9760. Resolving power, then is calculated using the formula,

$$\text{Resolving Power} = m/\ m = 380.9760/0.038 = 10025.$$

The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less. At a minimum, the ions listed in the method for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection of the molecular ions M and M+2 for ^{13}C-HxCDF and ^{13}C-HpCDF rather than M+2 and M+4 (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in the method. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors.

Static resolving checks must be performed at the beginning and at the end of each 12-hour shift. Raw data printouts of the mass resolving checks analyzed at the beginning and end of the 12-hour shift must be included in the data package. The injection time for the beginning mass resolution check that the laboratory submits as documentation of compliant instrument performance is considered to be the beginning of the 12-hour shift.

Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. An acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

3.1 Was mass calibration performed at the frequency given above?

3.2 Was the resolving power of PFK ion 380.9760 above 10000, when it was transmitted at the accelerating voltage corresponding to m/z ion 304.9824?

VALIDATION ACTION:
Qualify associated positive sample results and detection limits as approximate (UJ,J).

GC Column Performance Check Solution

The GC Column Performance Check solution must contain the first and the last isomers of each homologue PCDD/PCDF, (the internal and recovery standards are optional). The solution also should contain a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. All peaks must be labeled and identified on the Selected Ion Current Profiles (SICPs). In addition, the first and last eluters must be labeled with the letter F or L, as appropriate. The chromatographic separation between 2378-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of < 25%.

At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound.

Switching Times – Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60 m DB-5 column.

3.3 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of GC column performance check solution at the beginning of every 12 hour period. Was this performed accordingly?

VALIDATION ACTION: If the GC column performance check solution was not analyzed at the required frequency,
qualify associated positive sample results and detection limits as approximate (UJ,J).

3.4 Were all peaks labeled and identified on the Selected Ion Current Profiles (SICPs)?

VALIDATION ACTION:
Request corrected data from laboratory.

3.5 For DB-5 or equivalent, the peak separation between the unlabeled 2378-TCDD and the peaks representing any other TCDD isomer shall be resolved with a valley of < 25 percent. Was this criteria met?

Calculation: % Valley = (x/y) x (100)

Y = The peak height of 2,3,7,8-TCDD isomer

X = The distance from the baseline to the bottom of the valley between the adjacent peaks.

VALIDATION ACTION: If the percent valley criteria are not met, qualify all positive data J. Do not qualify detection limits.

3.6 Is the last eluting tetra chlorinated congener (1,2,8,9-TCDD) and the first eluting penta chlorinated congener (1,3,4,6,8-PeCDF) separated properly, since they elute within 15 seconds of each other?

VALIDATION ACTION: If one of the congener is missing, document in the validation report.

3.7 List below the samples qualified due to mass calibration or GC column performance excursions.

Mass resolution check ID	Excursion	Samples Affected (client/lab ID)	Action

4.0 INITIAL CALIBRATION

Criteria:

The initial calibration standard solutions (HRCC1-HRCC5) must be analyzed prior to any sample analysis. They do not have to be analyzed daily, provided the continuing calibration standard met all criteria. However, initial calibration should be analyzed at least once every week and/or whenever the continuing calibration standard does not meet all criteria. The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze the GC column performance check solution.
The total cycle time must be < 1 second (includes the sum of all the dwell times and voltage reset times).
The chromatographic resolution between the 2378-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of < 25 percent.
In the HRCC3 solution, the chromatographic peak separation between 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD shall be resolved with a valley of < 50 percent.
For all calibration solutions the retention times of the isomers must fall within the retention time windows established by the GC column performance check solution. In addition, the absolute retention times of recovery standards, 13C121234-TCDD and 13C12-123789HxCDD shall not change by more than 10 seconds between the HRCC3 analysis and the analysis of any other standard.
The two SIM ions for each homolog must maximize simultaneously and within 3 seconds of the corresponding labeled isomer ions.
The relative ion abundance criteria for PCDDs/PCDFs must be met.
The relative ion abundance criteria for the labeled internal and recovery standards must be met.
For all calibration solutions, including HRCC3, the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards must be > 10.
The percent relative standard deviations (% RSD) for the mean response factors (RRF) from the 17 unlabeled standards must not exceed + 20%, and those for the nine labeled reference compounds must not exceed + 30%.

Was the initial calibration performed at the frequency specified above?

Is mass calibration performed as described previously?

Is the total cycle time < 1 second?

Were SIM data acquired for each of the ions, including interfering ions?

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDF
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDF
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDF (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	TCDF
	[354.9792]	LOCK	C_9F_{13}	TCDF
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8250	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	423.7767	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7780	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[442.9728]	LOCK	$C_{10}F_{17}$	PFK

(b) The following nuclidic masses were used:

H	=	1.007825	0	=	15.994915
C	=	12.000000	^{35}Cl	=	34.968853
^{13}C	=	13.003355	^{37}Cl	=	36.965903
F	=	18.9984			

S = internal/recovery standard

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

(c) Used only for ^{13}C-HxCDF (IS)
(d) Used only for ^{13}C-HpCDF (IS)

VALIDATION ACTION:
1. If the 25% percent valley for TCDD and 50%valley for HxCDD requirement are not met, quality positive data (J). Do not qualify non-detects. The tetra, pentas and hexas (dioxins and furans) are affected. Heptas and Octas are not affected.
2. If the %RSD for each unlabeled isomer exceeds 20%,or the %RSD for each labeled isomer exceeds 30%, flag the associated sample positive results for that specific isomer as estimated ("J"). No effect on the non-detect data.
3. If the ion abundance ratio for an analyte is outside the limits, reject the results for that analyte (R).
4. If the ion abundance ratio for an internal or recovery standard falls outside the QC limits flag the associated positive hits with J. No effect on the non-detects.
5. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.
6. If the selected monitoring ions were not used for data acquisition, the lab must be asked for an explanation. If an incorrect ion was used, reject all the associated data.
7. If mass calibration criteria as previously described is not met, specify that in case narrative.
8. Non compliance of all other criteria specified above should be evaluated using professional judgement.

Spot check response factor calculations and ion ratios.
Ensure that the correct quantitation ions for the unlabeled PCDDs/PCDFs and internal standards were used.
Verify that the appropriate internal standard was used for each isomer.

To recalculate the response factor, use the equation:

$RRFn = [(An^1 + An^2) \times Qis] / [(Ais^1 + Ais^2) \times Qn]$

$RRFis = [(Ais^1 + Ais^2) \times Qrs] / [(Ars^1 + Ars^2) \times Qis]$

Where:

An^1 and An^2 = integrated areas of the two quantitation ions of isomer of interest.

Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.

Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.

Qn = quantity of the unlabeled PCDD/PCDF analyte injected (pg)

Qis = quantity of the appropriate internal standard injected (pg)

Qrs = quantity of the appropriate recovery standard injected (pg)

List below all initial calibrations and samples qualified due to initial calibration excursions.

Unique IC ID	Excursion	Samples Affected	Action

5.0 CONTINUING CALIBRATION

Criteria:

The continuing calibration must be performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A continuing calibration is also required at the end of a 12 hour shift.
The total cycle time is < 1 second.
SIM data are acquired for each of the ions including diphenylether interfering ions.
For the continuing calibration solution the retention time of the isomers must fall within the retention time windows established by the GC column performance check solution.
The absolute retention time of the recovery standards 13C121234-TCDD and 13C12123679-HxCDD shall not change by more than 10 seconds between the initial HRCC3 and ending HRCC3 standard analyses.
The two SIM ions for each homolog must maximize simultaneously (+ 2 sec) and within 3 seconds of the corresponding ions of the labeled isomers.
For the HRCC3 standard solution, the signal to noise ratio (S/N) for the unlabeled PCDD/PCDF ion shall be greater than 2.5.
For the internal standards and the recovery standards, the signal to noise ratio (S/N) shall be greater than 10.
The relative ion abundance criteria for all PCDD/PCDF shall be met.
The relative ion abundance criteria for all internal and recovery standards must be met.
The %Difference of RRF of each unlabeled analyte must be within +20 percent of the mean RRF established during the initial calibration. The measured RRFs for each of the labeled standards must be within + 30 percent of the mean RRF established during the initial calibration.

Was the same internal standard used to calculate RRF for each PCDD/PCDF homolog in the initial calibration?

Was the chromatographic peak separation on DB-5 (or equivalent) column between unlabeled 2378-TCDD and the peaks representing any other unlabeled TCDD isomers resolved with a valley of < 25 percent?

Was the chromatographic peak separation between the 123478-HxCDD and the 123678-HxCDD in the HRCC3 solution resolved with a valley of <50 percent?

Was the continuing calibration run at the required frequency?

VALIDATION ACTION:

1. If any of the requirements for total cycle time <1 second, SIM data acquired for each ion (including diphenylether), retention times for continuing calibration solution falling within windows, retention times for recovery standards (not changing more than 10 seconds), and using the same internal standard as in the initial calibration are not met, use professional judgement to determine the validity of the data.

2. If any requirements listed for ions maximizing within 2-3 seconds, S/N ratio in the HRCC3 standard, internal standards and recovery standards, relative ion abundance criteria for analytes, internal standards, and recovery standards are not met reject all data (R) directly affected by each specific problem.

3. When the %D of the RRF is in between 30% and 50%, all the data for the outlier congeners are flagged (J). Data with %D above 50% are rejected (R).

4. If the continuing calibration standard was not analyzed at the required frequency, reject all the data (R). Contact Project Manager to initiate reanalysis.

5. If the 25 percent valley and 50 percent valley criteria are not met, qualify all positive data with (J). Do not qualify non-detects. The tetras, pentas and hexas (dioxins and furans) are affected. Heptas and octas are not affected. If the percent valley is >75 percent and 2378-TCDD is non-detect but 1234-TCDD or an adjacent TCDD isomer is present, the data is questionable. The sample must be reanalyzed. Contact Project Manager. If the valley criteria for HxCDD are not met, but the valley criteria for TCDD are met or vice-versa, use professional judgement to determine which data must be qualified.

6. If the HRCC3 standard performed at the end of the 12 hour shift did not meet criteria specified in retention times of the isomers, S/N ratio in the HRCC3 standard, internal standards and recovery standards, relative ion abundance criteria for analytes, internal standards, and recovery standards, examine the samples which were analyzed prior to this standard and use professional judgement to determine if data qualification is necessary.

7.0 For all other criteria, use professional judgement.

Spot check response factor calculations and ion ratios. Verify that the appropriate quantitation ions for the unlabeled PCDD/PCDFs and internal standards were used.

To recalculate RRFs for the unlabeled target analytes, and the RRFs for the nine labeled internal standards, use the following equations:

$RRFn = [(An^1 + An^2) \times Qis] / [(Ais^1 + Ais^2) \times Qn]$
$RRFis = (Ais^1 + Ais^2) \times Qrs \; / \; [(Ars^1 + Ars^2) \times Qis]$
Where:
An^1 and An^2 = integrated areas of the two quantitation ions of isomer of interest.
Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.
Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.
Qn = quantity of the unlabeled PCDD/PCDF analyte injected (pg)
Qis = quantity of the appropriate internal standard injected (pg)
Qrs = quantity of the appropriate recovery standard injected (pg)

To calculate percent difference use the following equation:
$\% \text{ Difference} = [(RRFi - RRFc) \times 100] / [RRFi]$

Where:
RRFi = Relative response factor established during initial calibration
RRFc = Relative response factor established during continuing calibration

5.1 List below all continuing calibrations and samples qualified due to continuing calibration excursions.

Unique CC ID	Compound	Excursion	Action	Samples Affected (client, lab IDs)

6.0 SAMPLE DATA (IDENTIFICATION)

Criteria:

Were the following MS/DS conditions used?

The total cycle time was < 1 second.
SIM data were acquired for each of the ions including diphenylether interfering ions.

Were the following identification criteria met?

For the 2378 substituted isomers found present and for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard.

For the 2378 substituted isomer reported present, and for which a labeled standard does not exist, the relative time (RRT) of the analyte must be within +.005 RRT units of the RRT established by the continuing calibration standard (HRCC3).

For non-2378 substituted compounds (tetra through octa) found present, the retention time must be within the window established by the GC column performance check solution, for the corresponding homologue.

All specified ions for each PCDD/PCDF isomer and the labeled standards must be present in the SICP. The two SIM ions for the analyte, the internal standards and recovery standards must maximize simultaneously (+2 seconds).

The integrated ion current for each characteristic ion of the analyte identified as positive, must be at least 2.5 times background noise and must not have saturated the detector.

The integrated ion current for the internal and recovery standard characteristic ions must be at least 10 times background noise.

The relative ion abundance criteria for all PCDDs/PCDFs found present must be met.

The relative ion abundance criteria for the internal and recovery standards must be met.

The identification of a GC peak as a PCDF can only be made if no signal having a S/N > 2.5 is detected at the same time in the corresponding polychlorinated diphenyl ether channel.
Is the above condition met?

The analyte concentration must be within the calibration range. If not, dilution should have been made to bring the concentration within the calibration range.
Was the above criteria met?

The analytical method clearly states that samples containing analytes having concentrations higher than 10 times the upper MCLs should be analyzed using a less sensitive, high resolution GC/low resolution MS method.

VALIDATION ACTION:

1. Reject (R) all positive data for the analytes which do not meet criteria for retention times for 2378 substituted isomers and non-2378 substituted isomers, and the presence of all ions for each isomer labeled standards in the SICP.

2. If the criteria for the integrated ion current for each ion for the analytes being 2.5 times the background noise are not met but all other criteria are met, qualify all positive data of the specific analyte with J.

3. If the requirements for the integrated ion current for the internal and recovery standard ions being 10 times the background noise are not met but all other requirements are met qualify the positive data of the corresponding analytes as approximate (J).

4. If the analytes reported positive do not meet ion abundance criteria for analytes, reject (R) all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).

5. If the internal standards and recovery standards do not meet ion abundance criteria but they meet all other criteria flag all corresponding data with "J".

6. If PCDF is detected but an interfering PCDPE is also detected reject the PCDF data (R). The reported value of PCDF is changed to EMPC.

7. If the lab did not monitor for PCDPEs, qualify all positive furan data as approximate (J).

Spot check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate concentration and EMPC. Ensure that the proper PCDDs/PCDFs and internal standards were used.

To recalculate the concentration of individual PCDD/PCDF isomers in the sample use the following equation:

Non-Aqueous Matrices:
$Cn\ (pg/g) = [Qis \times (An1 + An2)]/[W \times (Ais1 + Ais2) \times RRFn]$

WATER
$Cn\ (ng/L) = [Qis \times (An^1 + An^2)]/[V \times (Ais^1 + Ais^2) \times RRFn]$

Where:
An^1 and An^2 = integrated ion abundances (peak areas) of the quantitation ions of the isomer of interest.
Ais^1 and Ais^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard.

W= Weight (g) of sample extracted
V= Volume (ml) of sample extracted
Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction
RRFn= Calculated relative response factor from continuing calibration.

6.1 List samples qualified due to identification excursions.

Sample ID (client/lab)	Compound	Excursion	Action

7.0 ESTIMATED DETECTION LIMITS (EDL)

Criteria:

The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

Samples giving a response for both quantitation ions that are less than 2.5 times the background level.

Use the expression for EDL to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions. of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that peak height.

Was an EDL calculated for each 2,3,7,8-substituted isomer that was not identified regardless of whether other non-2378 substituted isomers were present?

Use the equation below to check EDL calculations:

Non-Aqueous Matrices
$$EDL\ (pg/g) = [2.5 \times Qis \times (Hx^1 + Hx^2) \times D]/[W \times (His^1 + His^2) \times RRFn]$$

WATER
$$EDL\ (ng/L) = [2.5 \times Qis \times (Hx^1 + Hx^2) \times D]/[V \times (His^1 + His^2) \times RRFn]$$

Where:
Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.
His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.
D = dilution factor
Where:
W= Weight (g) of sample extracted
V= Volume (ml) of sample extracted
Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction
RRFn= Calculated relative response factor from continuing calibration.

VALIDATION ACTION:
Check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the laboratory for recalculation. The Project Manager must be notified.

8.0 ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC)

Criteria:

When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria, calculate the "**Estimated Maximum Possible Concentration**" (EMPC).

Was an EMPC calculated for 2378-substituted isomers that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria?

Use the equation below to check EMPC calculations:

Nonaqueous Matrices

EMPC (μg/L) = $[(Ax^1 + Ax^2) \times Qis \times D]/[(Ais^1 + Ais^2) \times RRFn \times W]$

WATER

EMPC (ng/L) = $[(Ax^1 + Ax^2) \times Qis \times D]/[(Ais^1 + Ais^2) \times RRFn \times V]$

Where:

Ax1 and Ax2 = areas of both quantitation ions.

Ais^1 and Ais^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard.

W= Weight (g) of sample extracted

V= Volume (ml) of sample extracted

Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction

RRFn= Calculated relative response factor from continuing calibration.

D is dilution factor.

VALIDATION ACTIONS:

1. If EDL or EMPC of an analyte which was not reported as present is missing, contact the laboratory for correction.

2. If the spot check calculations yielded EDLs or EMPCs different from those reported in Form I, contact the laboratory for an explanation.

3. If EDLs or EMPCs for the most toxic analytes (TEF> 0.05) are above CRQLs contact TPO for sample reanalysis.

Check EMPC calculation.

9.0 BLANK ANALYSIS (METHOD, RINSATE, FIELD)

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (parts per trillion)

	Water	Soil Sediment Paper Pulp[b]	Fly Ash	Fish Tissue[c]	Human Adipose Tissue	Sludges, Fuel Oil	Still-Bottom
Lower MCL[a]	0.01	1.0	1.0	1.0	1.0	5.0	10
Upper MCL[a]	2	200	200	200	200	1000	2000
Weight (g)	1000	10	10	20	10	2	1
IS Spiking Levels (ppt)	1	100	100	100	100	500	1000
Final Extract Volume (μL)[d]	10-50	10-50	50	10-50	10-50	50	50

a For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, by 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.

b Sample dewatered

c One half of the extract from the 20 g sample is used for determination of lipid content.

Method Blank
Criteria:
Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?

If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event?

Acceptable method blanks must not contain any signal of 2378-TCDD, or 2378-TCDF, equivalent to a concentration of > 20 ppt for soils or 0.2 ppt for water samples.
Is this criteria met?

For other 2378- substituted PCDD/PCDF isomers of each homologue, the allowable concentration in the method blank is less than 1/10 of the upper MCL of the method or the area must be less than 2% of the area of the nearest internal standard.
Is this criteria met?

For the peak which does not meet identification criteria as PCDD/PCDF in the method blank, the area must be less than 5% of the area of the nearest Internal Standard.
Was this condition met?

VALIDATION ACTION:
1. If the proper number of method blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the method blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD, 12378PeCDF or 23478 PeCDF at a concentration higher than the upper MCL, reject all contaminant compound positive data for the associated samples (R) and contact the Project Manager to initiate reanalysis if it is deemed necessary.
3. If the method blank is contaminated with any of the above isomers at a concentration of less than the upper MCL specified in the method or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

Rinsate Blank
Criteria:
One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent. Was rinsate blanks collected at the above frequency?
Do any rinsate blanks show the presence of 2378-TCDD, 2378-TCDF, and 12378PeCDD at amounts > .5 ug/L or any other analyte at levels > 1 ug/L?

VALIDATION ACTION:
1. If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the Project Manager to discuss what proper action must be taken.

Field Blanks
Criteria:
Note for Region V: Equipment/Field blanks are not used for qualification of samples.
The field blanks are blind blanks at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory. Acceptable field blanks must not contain any signal of 2378-TCDD, 2378-TCDF, 12378-PeCDD and 12378-PeCDF equivalent to a concentration of > 20 ppt.
For other 2378 substituted PCDD/PCDF isomers of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method.

9.1 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

10.0 INTERNAL STANDARDS EVALUATION

Criteria:

For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

1 Were the samples spiked with all the internal standards listed in the method?

2 Were internal standard recoveries within the required (40 - 135%) limits?

.3 If not, were samples reanalyzed?

VALIDATION ACTION:

1. If the internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.
2. If the internal standard recovery is above the upper limit (135 percent) flag all associated data (positive and non-detect data) with "J".
3. If the internal standard recovery is less than 10%, qualify all associated data reject (R) when highly toxic isomers (TEF> 0.05) are affected, notify Project Manager to initiate reanalysis.

Recalculate the percent recovery for internal standards in the sample extract, Ris, using the formula:

$Ris = [(Ais^1 + Ais^2) \times Qrs \times 100\%] / [(Ars^1 + Ars^2) \times RRFis \times Qis]$

Where:

Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.

Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.

Qis = quantity of the appropriate internal standard injected (pg)

Qrs = quantity of the appropriate recovery standard injected (pg)

RRFn= Calculated relative response factor from continuing calibration.

10.1 List samples qualified due to internal standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Action

11.0 RECOVERY STANDARDS

Criteria:
There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration?
Area upper limit= +100% of recovery standard area.
Area lower limit= -50% of recovery standard area.

Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?

VALIDATION ACTION:

1. If the recovery standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, reject all associated non-detect data (R) and flag the positive data (J).

3. If the retention time of the recovery standard differs by more than 10 seconds from the daily calibration use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the GC column performance check solution.

11.1 List samples qualified due to recovery standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Recovery Standard	Area and Percent Recovery	Action

12.0 MATRIX SPIKE

Criteria:

The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

12.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?

12.2 Was the percent recovery of 2378-TCDD and other 2378-substituted PCDDs/PCDFs within 50 to 150 percent?

VALIDATION ACTIONS:

If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 50-150% limits of the matrix spike data are used to flag data of the unspiked sample only; qualify sample results as approximate (UJ,J) if control limits are exceeded..

12.3 List samples qualified due to matrix spike excursions.

INSTRUMENT:

Matrix Spike ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

13.0 DUPLICATE SAMPLES

Criteria:
The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean).

For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency?

Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8 substituted isomers and 50% for the rest of the congeners?

VALIDATION ACTION:
The duplicate results must be used in conjunction of other QC data. Qualify detected sample results as approximate (J) if control limits are exceeded. If no hits are reported, precision is assessed from the internal standard recoveries.

13.1 List samples qualified due to duplicate excursions.

INSTRUMENT:

Duplicate ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

14.0 SECOND COLUMN CONFIRMATION

Criteria:

A high-resolution capillary column (60 m DB-5, J&W Scientific, or equivalent) is used in this method. However, no single column is known to resolve all isomers. The 60 m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity. In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent.

The concentration of the 2,3,7,8-TCDF is obtained from the analysis of the sample extract on the 30 m DB-225 fused silica capillary column. However, the GC/MS conditions must be altered so that: (1) only the first three descriptors (1.e., tetra-, penta-, and hexachlorinated congeners) are used; and (2) the switching time between descriptor 2 (pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}C_{12}$-1,2,3,7,8-PeCDD. The chromatographic separation between the 2,3,7,8-TCDF and its close eluters (2,3,4,7-TCDF and 1,2,3,9-TCDF must be equal or less than 25 percent valley.

Was a second column confirmation performed?
Was the sample extract reanalyzed on a 30 m DB-225, fused silica capillary column, for 2,3,7,8 TCDF using the GC/MS conditions given in **Section 7.9.7.1.2 of the analytical method?**

The concentration of 2,3,7,8 TCDF obtained from the primary column (DB-5) should only be used for qualification, due to better QC data associated with the primary column. Also note that the confirmation and quantitation of 2,3,7,8-TCDD may be accomplished on a SP-2330 GC column.

VALIDATION ACTIONS:
If confirmation is missing, use professional judgement, or contact Project Manager for assistance.

1 Did the second column meet the initial calibration and continuing calibration specifications as previously described?

2 Was the % D of the quantitation results of the two columns less than 50?

14.1 List samples affected by second column confirmation excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Analyte	Excursion	Action

15.0 SAMPLE REANALYSIS

Criteria:

Due to a variety of situations that may occur during sample analysis the laboratory is required to reanalyze or reextract and reanalyze certain samples.

VALIDATION ACTIONS:
If a reanalysis was required but was not performed, contact Project Manager to initiate reanalysis. List below all reextractions and reanalyses and identify the PCDD/PCDF sample data summaries, which must be used by the data user (when more than one is submitted).

15.1 List samples affected by sample reanalysis excursions.

INSTRUMENT:

Sample ID (client/lab)	Analyte	Excursion	Action

16.0 TOXICITY EQUIVALENCY FACTOR (TEF)

Criteria:

The 2,3,7,8-TCDD **toxicity equivalents** (TE) of PCDDs and PCDFs present in the sample are calculated. This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDD and PCDFs and to OCDD and OCDF. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds.

When calculating the 2378-TCDD Toxicity Equivalency of a sample only those 2378 substituted isomers that were positively identified in the sample must be included in the calculations. The sum of the TEF adjusted concentration is used to determine when a second column confirmation is required to achieve isomer specificity.

Did the lab include EMPC or EDL values in the toxicity equivalency calculations?

Were all samples, whose toxicity equivalency exceeded the required values were reanalyzed on a confirmation column to establish isomer specificity?

VALIDATION ACTION:

1. If the toxicity equivalency calculations were not performed properly notify TPO.

2. If the toxicity equivalency exceeded the required limits (0.7 ppb for soil/sediment, 7ppt for aqueous and 7ppb for chemical waste samples), and the lab failed to reanalyze the samples on a specific secondary column, notify the Project Manager.

16.1 List samples affected by TEF excursions.

Instrument:

Sample ID	Analyte	Excursion	Action

17.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

17.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form

USEPA Method 8290 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS

Date:____________________ Number of samples and compounds per sample:______________

Project Number:____

Validator:____Equipment Blanks:________

Project: ____Blind/Field Duplicates:______

Laboratory:____MS/MSDs:____________

QAPP:__________________________________ DV Guidelines: USEPA Region II

Laboratory package number:_________________PARTIAL VALIDATION

Method reference:

- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, 3rd Edition. Washington D.C.*

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8290	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8290	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms

Method 8290 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS

The following worksheets are based on:

- USEPA. 1994 *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS).* Albany, New York.
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, 3rd Edition. Washington D.C.*

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VALIDATION DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the qualifiers assigned to results in the data validation process.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

U - Not detected above the reported detection limit.

NJ - There is presumptive evidence for the presence of the compound at an estimated value.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is Not Reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR DIOXIN/DIBENZOFURAN ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues with sample receipt or condition of samples.

1.2 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.3 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.4 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.5 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

Criteria:

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Holding times for PCDD/PCDF:
Aqueous and solid samples – 30 days from collection to extraction, 45 days from extraction to analysis.

The holding times for extraction/preparation presented in Method 8290 are considered to be contractual holding times only. There are no demonstrated maximum holding times associated with the extraction/preparation of PCDDs/PCDFs in aqueous, solid, semi-solid, tissues, and other sample matrices. If samples are stored properly, the holding times for extraction/preparation are up to one year. Sample extracts are to be analyzed within 45 days of preparation.

VALIDATION ACTION:
If holding times for analysis of sample extracts are exceeded, positive results and detection limits are considered to be approximate (UJ, J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 BLANK ANALYSIS (METHOD, RINSATE, FIELD)

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD-Based Method Calibration Limits (parts per trillion)

	Water	Soil Sediment Paper Pulp[b]	Fly Ash	Fish Tissue[c]	Human Adipose Tissue	Sludges, Fuel Oil	Still-Bottom
Lower MCL[a]	0.01	1.0	1.0	1.0	1.0	5.0	10
Upper MCL[a]	2	200	200	200	200	1000	2000
Weight (g)	1000	10	10	20	10	2	1
IS Spiking Levels (ppt)	1	100	100	100	100	500	1000
Final Extract Volume (μL)[d]	10-50	10-50	50	10-50	10-50	50	50

a For other congeners multiply the values by 1 for TCDF/PeCDD/PeCDF, by 2.5 for HxCDD/HxCDF/HpCDD/HpCDF, and by 5 for OCDD/OCDF.
B Sample dewatered
c One half of the extract from the 20 g sample is used for determination of lipid content.

Method Blank
Criteria:
Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?

If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event?

Acceptable method blanks must not contain any signal of 2378-TCDD, or 2378-TCDF, equivalent to a concentration of > 20 ppt for soils or 0.2 ppt for water samples.
Is this criteria met?

For other 2378- substituted PCDD/PCDF isomers of each homologue, the allowable concentration in the method blank is less than 1/10 of the upper MCL of the method or the area must be less than 2% of the area of the nearest internal standard.
Is this criteria met?

For the peak which does not meet identification criteria as PCDD/PCDF in the method blank, the area must be less than 5% of the area of the nearest Internal Standard.
Was this condition met?

VALIDATION ACTION:
1. If the proper number of method blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the method blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD, 12378PeCDF or 23478 PeCDF at a concentration higher than the upper MCL, reject all contaminant compound positive data for the associated samples (R) and contact the Project Manager to initiate reanalysis if it is deemed necessary.
3. If the method blank is contaminated with any of the above isomers at a concentration of less than the upper MCL specified in the method or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

Rinsate Blank
Criteria:
One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent. Was rinsate blanks collected at the above frequency?
Do any rinsate blanks show the presence of 2378-TCDD, 2378-TCDF, and 12378PeCDD at amounts > .5 ug/L or any other analyte at levels > 1 ug/L?

VALIDATION ACTION:
1. If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the Project Manager to discuss what proper action must be taken.

Field Blanks
Criteria:
Note for Region V: Equipment/Field blanks are not used for qualification of samples.
The field blanks are blind blanks at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory. Acceptable field blanks must not contain any signal of 2378-TCDD, 2378-TCDF, 12378-PeCDD and 12378-PeCDF equivalent to a concentration of > 20 ppt.
For other 2378 substituted PCDD/PCDF isomers of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method.

3.1 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

4.0 INTERNAL STANDARDS EVALUATION

Criteria:

For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

1 Were the samples spiked with all the internal standards listed in the method?

2 Were internal standard recoveries within the required (40 - 135%) limits?

.3 If not, were samples reanalyzed?

VALIDATION ACTION:

1. If the internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.
2. If the internal standard recovery is above the upper limit (135 percent) flag all associated data (positive and non-detect data) with "J".
3. If the internal standard recovery is less than 10%, qualify all associated data reject (R) when highly toxic isomers (TEF> 0.05) are affected, notify Project Manager to initiate reanalysis.

4.1 List samples qualified due to internal standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Action

5.0 RECOVERY STANDARDS

For partial validation, the recovery standard is reviewed if recoveries are presented in a summary form.

Criteria:
There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration?
Area upper limit= +100% of recovery standard area.
Area lower limit= -50% of recovery standard area.

Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?

VALIDATION ACTION:

1. If the recovery standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, reject all associated non-detect data (R) and flag the positive data (J).

3. If the retention time of the recovery standard differs by more than 10 seconds from the daily calibration use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the GC column performance check solution.

5.1 List samples qualified due to recovery standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Recovery Standard	Area and Percent Recovery	Action

6.0 MATRIX SPIKE

Criteria:

The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?

.2 Was the percent recovery of 2378-TCDD and other 2378-substituted PCDDs/PCDFs within 50 to 150 percent?

VALIDATION ACTIONS:
If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 50-150% limits of the matrix spike data are used to flag data of the unspiked sample only; qualify sample results as approximate (UJ,J) if control limits are exceeded.

6.1 List samples qualified due to matrix spike excursions.

INSTRUMENT:

Matrix Spike ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

7.0 DUPLICATE SAMPLES

Criteria:

The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean).

For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency?

Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8 substituted isomers and 50% for the rest of the congeners?

VALIDATION ACTION:

The duplicate results must be used in conjunction of other QC data. Qualify detected sample results as approximate (UJ,J) if control limits are exceeded. If no hits are reported, precision is assessed from the internal standard recoveries.

7.1 List samples qualified due to duplicate excursions.

INSTRUMENT:

Duplicate ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

Section 9

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8280A Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS (High Resolution GC/Low Resolution MS) – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method 8280A Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS (High Resolution GC/Low Resolution MS) – Partial Validation

O'Brien & Gere Engineers Data Validation Form
USEPA Method 8280A Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS (High Resolution GC/Low Resolution MS)

Date:____________________ **Number of samples and compounds per sample:**_______________

Project Number:____

Validator:____**Equipment Blanks:**_______

Project: ____**Blind/Field Duplicates:**_____

Laboratory:____**MS/MSDs:**_____________

QAPP:_________________________________ **DV Guidelines: USEPA Region II**

Laboratory package number:_________________**FULL VALIDATION**

Method reference:

- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, 3rd Edition. Washington D.C.*

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8280A	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8280A	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms

Method 8280A Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS

The following worksheets are based on:

- USEPA. 1994 *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)*, Albany, New York. (Edited for 8280A)
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd Edition. Washington D.C.*

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VALIDATION DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the qualifiers assigned to results in the data validation process.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

U - Not detected above the reported detection limit.

NJ - There is presumptive evidence for the presence of the compound at an estimated value.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

Method 8280A Information

1.1 This method is appropriate for the detection and quantitative measurement of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCDD), 2,3,7,8-tetrachlorinated dibenzofuran (2,3,7,8-TCDF), and the 2,3,7,8-substituted penta-, hexa-, hepta-, and octachlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in water (at part-per-trillion concentrations), soil, fly ash, and chemical waste samples, including stillbottoms, fuel oil, and sludge matrices (at part-per-billion concentrations).

1.2 The analytical method requires the use of high resolution gas chromatography and low resolution mass spectrometry (HRGC/LRMS) on sample extracts that have been subjected to specified cleanup procedures.

1.3. If the toxicityequivalence is greater than or equal to 0.7 ppb (soil or fly ash), 7 ppt (aqueous), or 7 ppb (chemical waste), analysis on a column capable of resolving all 2,3,7,8-substituted PCDDs/PCDFs is necessary. If the expected concentrations of the PCDDs and PCDFs are below the quantitation limits, use of Method 8290 may be more appropriate.

1.4 This method contains procedures for reporting the total concentration of all PCDDs/PCDFs in a given level of chlorination, although complete chromatographic separation of all 210 possible PCDDs/PCDFs is not possible under the instrumental conditions described here.

2.0 SUMMARY OF THE METHOD
2.1 Matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) techniques.

2.2 If interferants are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination.

2.3 A specified amount of water, soil, fly ash, or chemical waste samples is spiked with internal standards and extracted according to a matrix-specific extraction procedure. Aqueous samples are filtered, and solid samples that show an aqueous phase are centrifuged before extraction.

2.4 The extracts are spiked with $^{37}Cl_4$ -2,3,7,8-TCDD and submitted to an acid-base washing treatment, dried and concentrated. The extracts are cleaned up by column chromatography on alumina, silica gel, and activated carbon on Celite 545® and concentrated again.

2.5 An aliquot of the concentrated extract is injected into an HRGC/LRMS system capable
of performing the selected ion monitoring.

2.6 The identification of the target compounds is based on their ordered elution and comparison to standard solutions. Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on a single column. The use of both DB-5 and SP2331 (or equivalent) columns is advised.

4.1.2.1 Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 column. Problems have been associated with the separation of 2,3,7,8-TCDD from 1,2,3,7-TCDD and 1,2,6,8-TCDD, and separation of 2,3,7,8-TCDF from 1,2,4,9-, 1,2,7,9-, 2,3,4,6-, 2,3,4,7-, and 2,3,4,8-TCDF. Because of the toxicologic concern associated with 2,3,7,8-TCDD and 2,3,7,8-TCDF, additional analyses may be necessary for some samples. In instances where the toxicity equivalent concentration (TEQ) is greater than 0.7 ppb (solids), 7 ppt (aqueous), or 7 ppb (chemical waste), the reanalysis of the sample extract on a 60 m SP-2330 or SP-2331 GC, or DB-225 column (or equivalent column) may be required in order to determine the concentrations of the individual 2,3,7,8-substituted isomers. For the DB-225 column, problems are associated with the separation of 2,3,7,8-TCDF from 2,3,4,7-TCDF and a combination of 1,2,3,9- and 2,3,4,8-TCDF.

4.2 Mass spectrometer - A low resolution instrument is employed, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM). The recommended configuration is for at least 18 ions per cycle, with a cycle time of 1 sec or less, and a minimum integration time of 25 msec per m/z.

5.9 Calibration solutions - five tridecane (or nonane) solutions (CC1-CC5) containing 10 unlabeled and 7 carbon-labeled PCDDs/PCDFs at known concentrations for use in instrument calibration. One of these five solutions (CC3) is used as the calibration verification solution and contains 7 additional unlabeled 2,3,7,8-isomers. The concentration ranges are homologue-dependent, with the lowest concentrations associated with tetra- and pentachlorinated dioxins and furans (0.1 to 2.0 ng/μL), and the higher concentrations associated with the hexa-through octachlorinated homologues (0.5 to 10.0 ng/μL).

5.10 Internal standard - five internal standards in tridecane

5.11 Recovery standard - a solution in hexane containing the recovery standards, $^{13}C_{12}$ -1,2,3,4-TCDD and $^{13}C_{12}$ -1,2,3,7,8,9-HxCDD, at concentrations of 5.0 ng/μL

5.12 Calibration verification solution – Prepare a solution containing standards to be used for identification and quantitation of target analytes (Table 4).

5.13 Cleanup standard - Prepare a solution containing $^{37}Cl_4$ -2,3,7,8-TCDD at a concentration of 5 ng/μL (5 μg/mL) in tridecane (or nonane). Add this solution to all sample extracts prior to cleanup. The solution may be added at this concentration, or diluted into a larger volume of solvent. The recovery of this compound is used to judge the efficiency of the cleanup procedures.

5.14 Matrix spiking standard - containing ten of the 2,3,7,8-substituted isomers, at the concentrations

5.15 Window defining mix - a solution containing the first and last eluting isomer of each homologue

6.3. Holding Times
PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions may be as high as a year for certain matrices. Sample extracts, however, should always be analyzed within 45 days of extraction.

7.11. Final Concentration

The final extract volume should be 100 µL of tridecane (or nonane).

7.12. Chromatographic conditions

On the DB-5 column,the chromatographic resolution is evaluated using the CC3 calibration standard during both the initial calibration and the calibration verification. The chromatographic peak separation between the $^{13}C_{12}$ -2,3,7,8-TCDD peak and the $^{13}C_{12}$ -1,2,3,4- TCDD peak must be resolved with a valley of ≤25 percent, where:

$$\text{Valley} = (x/y) \times 100$$

y = the peak height of any TCDD isomer
x = measured as shown in Figure 2

The resolution criteria must be evaluated using measurements made on the selected ion current profile (SICP) for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

7.12.2 When an SP-2331 (or equivalent) GC column is used to confirm the results for 2,3,7,8-TCDF, the chromatographic resolution is evaluated before the analysis of any calibration standards by the analysis of a commercially-available column performance mixture that contains the TCDD isomers that elute most closely with 2,3,7,8-TCDD on this GC column (1,4,7,8-TCDD and the 1,2,3,7/1,2,3,8-TCDD pair). Analyze a 2-µL aliquot of this solution, using the column operating conditions and descriptor switching times previously established. The GC operating conditions for this column should be modified from those for the DB-5 (or equivalent) column, focusing on resolution of the closely-eluting TCDD and TCDF isomers.

NOTE: The column performance mixture may be combined with the window defining mix

The chromatographic peak separation between unlabeled 2,3,7,8-TCDD and the peaks representing all other unlabeled TCDD isomers should be resolved with a valley of ≤25 percent.

7.13 GC/MS Calibration
Calibration of the GC/MS system involves three separate procedures, mass calibration of the MS, establishment of GC retention time windows, and calibration of the target analytes.

7.13.1 Mass calibration - Mass calibration of the MS is recommended prior to analyzing the calibration solutions, blanks, samples and QC samples. It is recommended that the instrument be tuned to greater sensitivity in the high mass range in order to achieve better response for the later eluting compounds. Optimum results using FC-43 for mass calibration may be achieved by scanning from 222-510 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode. Under these conditions, m/z 414 and m/z 502 should be 30-50% of m/z 264 (base peak).

7.13.2 Retention time windows - Prior to the calibration of the target analytes, it is necessary to establish the appropriate switching times for the SIM descriptors. The switching times are determined by the analysis of the Window Defining Mix, containing the first and last eluting isomers in each homologue. Mixes are available for various columns.

The ions in each of the four recommended descriptors are arranged so that there is overlap between the descriptors. The ions for the TCDD, TCDF, PeCDD, and PeCDF isomers are in the first descriptor, the ions for the PeCDD, PeCDF, HxCDD and HxCDF isomers are in the second descriptor, the ions for the HxCDD, HxCDF, HpCDD and HpCDF isomers are in the third, and the ions for the HpCDD, HpCDF, OCDD and OCDF isomers are in the fourth descriptor.

7.13.3 Calibration of target analytes - The initial
calibration is needed before any samples are analyzed for PCDDs/PCDFs, and intermittently throughout sample analysis, as dictated by the results of the calibration verification. The calibration verification is necessary at the beginning of each 12-hour time period during which sample are analyzed.

7.13.3.1 Initial Calibration - Once the Window Defining Mix has been analyzed and the descriptor switching times have been verified (and after the analysis of the column performance solution, if using a GC column other than DB-5), analyze the five concentration calibration solutions (CC1-CC5), described in Table 1, prior to any sample analysis.

7.13.3.1.1 The relative ion abundance criteria for PCDDs/PCDFs presented should be met for all PCDD/PCDF peaks in all solutions. The $^{37}Cl_4$ -2,3,7,8-TCDD cleanup standard contains no ^{35}Cl, thus the ion abundance ratio criterion does not apply to this compound.

Calculate the RFs for the five labeled internal standards

$$RF_n = (A_n^1 + A_n^2) \times Q_{is}$$

$$(A_{is}^1 + A_{is}^2) \times Q_n$$

$$RF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

where:

A_n^1 and A_n^2	=	integrated areas of the two quantitation ions of the isomer of interest
A_{is}^1 and A_{is}^2	=	integrated areas of the two quantitation ions of the appropriate internal standard
A_{rs}^1 and A_{rs}^2	=	integrated areas of the two quantitation ions of the appropriate recovery standard
Q_n	=	nanograms of unlabeled target analyte injected
Q_{is}	=	nanograms of appropriate internal standard injected
Q_{rs}	=	nanograms of appropriate recovery standard injected

7.13.3.3 Relative response factors for the unlabeled PCDDs/PCDFs relative to the recovery standards (RF_{rs}), where:

$$RF_{rs} = RF_n \times RF_{is}$$

This relative response factor is necessary when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

7.13.3.4 - Calculate the mean RF and percent relative standard deviation (%RSD) of the five RFs (CC1 to CC5) for each unlabeled PCDD/PCDF and labeled internal standards present in all five concentration calibration solutions. No mean RF or %RSD calculations are possible for the 2,3,7,8-substituted isomers or the cleanup standard found only in the CC3 solution.

The %RSD of the five RFs (CC1-CC5) for the unlabeled PCDDs/PCDFs and the internal standards should not exceed 15.0%.

7.13.3.6 Calibration Verification - The calibration verification consists of two parts: evaluation of the chromatographic resolution, and verification of the RF values to be used for quantitation. At the beginning of each 12-hour period, the chromatographic resolution is verified in the same fashion as in the initial calibration, through the analysis of the CC3 solution on the DB-5 (or equivalent) column, or through the analysis of the column performance solution on the SP-2331 (or equivalent) column.

1) GC Column Resolution Criteria - The chromatographic resolution on the DB-5 (or equivalent) and /or the SP-2331 (or equivalent) column must meet the QC criteria. In addition, the chromatographic peak separation between the 1,2,3,4,7,8-HxCDD and the 1,2,3,6,7,8-HxCDD in the CC3 solution shall be resolved with a valley of ≤50 percent.

2) Ion Abundance Criteria - The relative ion abundances must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards.

3) Instrument Sensitivity Criteria - For the CC3 solution, the signal-to-noise (S/N) ratio shall be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10.0 for the labeled internal and recovery standards.

4) Response Factor Criteria - The measured RFs of each analyte and internal standard in the CC3 solution must be within ±30.0% of the mean RFs established during initial calibration for the analytes in all five calibration standards, and within ±30.0% of the single-point RFs established during initial calibration for those analytes present in only the CC3 standard

7.13.3.7 In order to demonstrate that the GC/MS system has retained adequate sensitivity during the course of sample analyses, the lowest standard from the initial calibration is analyzed at the end of each 12-hour time period during which samples are analyzed.

The results of this analysis must meet the acceptance criteria for retention times, ion abundances, and S/N ratio for the continuing calibration standard. Response factors do not need to be evaluated in this end-of-shift standard. If this analysis fails either the ion abundance or S/N ratio criteria, then any samples analyzed during that 12-hour period that indicated the presence of any PCDDs/PCDFs below the method quantitation limit or where estimated maximum possible concentrations were reported must be reanalyzed. Samples with positive results above the method quantitation limit need not be reanalyzed.

GC/MS analysis of samples

Inject a 2-µL aliquot of the extract into the GC/MS instrument.

7.14.4 Dilution of the sample extract is necessary if the concentration of any PCDD/PCDF in the sample has exceeded the calibration range, or the detector has been saturated. An appropriate dilution will result in the largest peak in the diluted sample falling between the mid-point and high-point of the calibration range.

7.14.4.1 Dilutions are performed using an aliquot of the original extract, of which approximately 50 µL remain. Remove an appropriate size aliquot from the vial and add it to a sufficient volume of tridecane (or nonane) in a clean 0.3-mL conical vial. Add sufficient recovery standard solution to yield a concentration of 0.5 ng/µL. Reduce the volume of the extract back down to 50 µL using a gentle stream of dry nitrogen.

7.14.4.2 The dilution factor is defined as the total volume of the sample aliquot and clean solvent divided by the volume of the sample aliquot that was diluted.

7.14.4.4 Diluted samples in which the MS response of any internal standard is greater than or equal to 10% of the MS response of that internal standard in the most recent calibration verification standard are quantitated using the internal standards. Diluted samples in which the MS response of any internal standard is less than 10% of the MS response of that internal standard in the most recent calibration verification standard are quantitated using the recovery standards.

7.14.5 Identification Criteria –

7.14.5.1 Retention times - In order to make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time (RT) at the maximum peak height of the analyte must be within -1 to +3 seconds of the retention time of the corresponding labeled standard. In order to make a positive identification of the 2,3,7,8-substituted isomers for which a labeled standard is *not* available, the relative retention time (RRT) of the analyte must be within 0.05 RRT units of the RRT established by the calibration verification. The RRT is calculated as follows:

$$\text{RRT} = \frac{\text{retention time of the analyte}}{\text{retention time of the corresponding internal standard}}$$

For non-2,3,7,8-substituted compounds (tetra through hepta), the retention time must be within the retention time windows established by the window defining mix for the corresponding homologue

The absolute retention times of the two recovery standards added to every sample extract immediately prior to analysis may not shift by more than ±10 seconds from their retention times in the calibration verification standard.

All of the ions for each PCDD/PCDF homologue and labeled standards must be present in the SICP. The ion current response for the two quantitation ions and the M-[COCL]$^+$ ions for the analytes must maximize simultaneously (±2 seconds). This requirement also applies to the internal standards and recovery standards. For the cleanup standard, only one ion is monitored.

7.14.5.3 Signal-to-noise ratio - The integrated ion current for each analyte ion must be at least 2.5 times background noise and must not have saturated the detector (Figure 4). The internal standard ions must be at least 10.0 times background noise and must not have saturated the detector. However, if the M-[COCL]$^+$ ion does not meet the 2.5 times S/N requirement but meets all the other criteria and, in the judgement of the GC/MS Interpretation Specialist the peak is a PCDD/PCDF, the peak may be reported as positive and the data flagged on the report form.

7.14.5.4 Ion abundance ratios - The relative ion abundance criteria for unlabeled analytes and internal standards must be met using peak areas to calculate ratios.

7.14.5.4.1 If interferences are present, and ion abundance ratios are not met using peak areas, but all other qualitative identification criteria are met (RT, S/N, presence of all 3 ions), then use peak heights to evaluate the ion ratio.

7.14.5.5 Polychlorinated diphenyl ether (PCDPE) interferences.

The identification of a GC peak as a PCDF cannot be made if a signal having S/N greater than 2.5 is detected at the same retention time (±2 seconds) in the corresponding PCDPE channel. If a PCDPE is detected, an Estimated Maximum Possible Concentration (EMPC) should be calculated for this GC peak regardless of the ion abundance ratio, and reported.

7.15 Calculations

7.15.1 For GC peaks that have met all the identification criteria, calculate the concentration of the individual PCDD or PCDF isomers using the formulae:

ALL MATRICES OTHER THAN WATER:

$$C_n\ (\mu g/kg) = \frac{Q_{is} \times (A_n^1 + A_n^2)}{W \times (A_{is}^1 + A_{is}^2) \times RF_n}$$

WATER:

$$C_n \text{ (ng/L)} = \frac{Q_{is} \times (A_n^1 + A_n^2)}{V \times (A_{is}^1 + A_{is}^2) \times RF_n}$$

where:

A_n^1 and A_n^2	=	integrated ion abundances (peak areas) of the quantitation ions of the isomer of interest
A_{is}^1 and A_{is}^2	=	integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard
C_n	=	concentration of unlabeled PCDD/PCDF found in the sample.
W	=	weight of sample extracted, in grams.
V	=	volume of sample extracted, in liters.
Q_{is}	=	nanograms of the appropriate internal standard added to the sample prior to extraction.
RF_n	=	calculated relative response factor from calibration verification

NOTE: In instances where peak heights are used to evaluate ion abundance ratios due to interferences, substitute peak heights for areas in the formulae above.

For solid matrices, the units of ng/g that result from the formula above are equivalent to µg/kg. Using isotope dilution techniques for quantitation the concentration data are recovery corrected, and therefore, the volume of the final extract and the injection volume are implicit in the value of Q_{is}

7.15.1.1 For homologues that contain only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the RF of the 2,3,7,8-substituted isomer from the calibration verification will be used to quantitate both the 2,3,7,8-substituted isomers and the non-2,3,7,8-isomers.

7.15.1.2 For homologues that contain *more than* one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF, and HpCDF), the RF used to calculate the concentration of each 2,3,7,8-substituted isomers will be the RF determined for that isomer during the calibration verification.

7.15.1.3 For homologues that contain one or more non-2,3,7,8-substituted isomer, the RF used to calculate the concentration of these isomers will be the lowest of the RFs determined during the calibration verification for the 2,3,7,8-substituted isomers in that homologue. This RF will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.

7.15.2 Calculate the total concentration of each homologue of PCDDs/PCDFs as follows:

Total concentration = sum of the concentrations of every positively identified isomer of each PCDD/PCDF homologue.

The total must include the non-2,3,7,8-substituted isomers as well as the 2,3,7,8-substituted isomers that are also reported separately.

7.15.3 If the area of any internal standard in a diluted sample is less than 10% of the area of that internal standard in the calibration verification standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the recovery standard, using the formulae that follow.

ALL MATRICES OTHER THAN WATER:

$$C_n \text{ (µg/kg)} = \frac{Q_{rs} \times (A_n^1 + A_n^2) \times D}{W \times (A_{rs}^1 + A_{rs}^2) \times RF_{rs}}$$

WATER:

$$C_n \text{ (ng/L)} = \frac{Q_{rs} \times (A_n^1 + A_n^2) \times D}{V \times (A_{rs}^1 + A_{rs}^2) \times RF_{rs}}$$

where:

D = the dilution factor
A_n^1, A_n^2, A_{rs}^1, A_{rs}^2, Q_{rs}, RF_{rs}, W, and V were previously defined

7.15.5 Calculate the percent recovery, R_{is}, for each internal standard and the cleanup standard in the sample extract, using the formula:

$$R_{is} (\%) = (A_{is}^1 + A_{is}^2) \times Q_{rs} \quad \times \quad 100$$

$$(A_{rs}^1 + A_{rs}^2) \times RF_{is} \times Q_{is}$$

where:

A_{is}^1, A_{is}^2, A_{rs}^1, A_{rs}^2, Q_{is}, Q_{rs}, and RF_{is}, were previously defined

7.15.5.1 The $^{13}C_{12}$ -1,2,3,4-TCDD is used to quantitate the TCDD and TCDF internal standards and the cleanup standard, and the $^{13}C_{12}$ -1,2,3,7,8,9-HxCDD is used to quantitate the HxCDD, HpCDF and OCDD internal standards.

7.15.5.2 If the original sample, prior to any dilutions, has any internal standard with a percent recovery of less than 25% or greater than 150%, re-extraction and reanalysis of that sample is necessary.

7.15.6 Estimated detection limit - The estimated detection limit (EDL) is the estimate made by the laboratory of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

7.15.6.1 An EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for 2,3,7,8-substituted isomers giving responses for both the quantitation ions that are less than 2.5 times the background level.

7.15.6.2 The background level (H_n) is determined by measuring the height of the noise at the expected retention times of both the quantitation ions of the particular 2,3,7,8-substituted isomer.

ALL MATRICES OTHER THAN WATER:

$$EDL\ (\mu g/kg) = \frac{2.5 \times Q_{is} \times (H_n^1 + H_n^2) \times D}{W \times (H_{is}^1 + H_{is}^2) \times RF_n}$$

WATER:

$$EDL\ (ng/L) = \frac{2.5 \times Q_{is} \times (H_n^1 + H_n^2) \times D}{V \times (Hi_s^1 + H_{is}^2) \times RF_n}$$

where:

H_n^1 and H_n^2	=	The peak heights of the noise for both of the quantitation ions of the 2,3,7,8-substituted isomer of interest
H_{is}^1 and H_{is}^2	=	The peak heights of both the quantitation ions of the appropriate is internal standards
D	=	dilution factor

Q_{is} , RF_{is} , W and V were previously defined

7.15.6.3 If none of the isomers within a homologue are detected, then the EDL for the "total" homologue concentration is the <u>lowest</u> EDL for any of the 2,3,7,8-substituted isomers that were not detected. Do <u>not</u> add together the EDLs for the various isomers. If a 2,3,7,8-substituted isomer <u>is</u> reported in the homologue, then no EDL for the "total" is calculated.

7.15.7 Estimated maximum possible concentration – An estimated maximum possible concentration (EMPC) is calculated for 2,3,7,8-substituted isomers that are characterized by a response with an S/N of at least 2.5 for both the quantitation ions, and meet all of the identification criteria <u>except</u> the ion abundance ratio criteria <u>or</u> when a peak representing a PCDPE has been detected. An EMPC is a worst-case estimate of the concentration. Calculate the EMPC according to the
following formulae:

ALL MATRICES OTHER THAN WATER:

$$EMPC_n\ (\mu g/kg) = Q_{is} \times (A_n^1 + A_n^2) \times D$$

$$W \times (A_{is}^1 + A_{is}^2) \times RF_n$$

WATER:

$$EMPC_n \text{ (ng/L)} = \frac{Q_{is} \times (A_n^1 + A_n^2) \times D}{V \times (A_{is}^1 + A_{is}^2) \times RF_n}$$

where:

A_x^1 and A_x^2 = Areas of both the quantitation ions

A_{is}^1, A_{is}^2, Q_{is}, RF_n, D, W, and V were previously defined

7.15.8 Toxic equivalent concentration (TEQ) calculation

7.15.8.1 The 2,3,7,8-TCDD TEQ of the PCDDs/PCDFs present in the sample is calculated by summing the product of the concentration for each of the compounds and the TEF for each compound.

Only the 2,3,7,8-substituted isomers are included in the TEF calculations.

Do not include EMPC or EDL values in the TEQ calculation.

7.15.8.2.1 If the TEQ is greater than 0.7 ppb for soil/sediment or fly ash, 7 ppb for chemical waste, or 7 ppt for an aqueous sample, and 2,3,7,8-TCDF is either detected or reported as an EMPC, then better isomer specificity may be required than can be achieved on the DB-5 column.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Sec. 8 of Method 8000 for information on developing acceptance criteria for the LCS.

8.4.3.1 Method blanks should be prepared at a frequency of at least 5%, that is, one method blank for each group of up to 20 samples prepared at the same time, by the same procedures.

8.4.3.2 The method blank must also be subjected to the same cleanup procedures.

8.4.3.4 the results of the method blank should be:

8.4.3.4.1 Less than the MDL for the analyte.

8.4.3.4.2 Less than 5% of the regulatory limit associated with an analyte.

8.4.3.4.3 Or less than 5% of the sample result for the same analyte, whichever is greater.

Table 1
CALIBRATION SOLUTIONS

Analyte	**Concentration of Standard in ng/μL** CC1	CC2	CC3	CC4	CC5
2,3,7,8-TCDD	0.1	0.25	0.5	1.0	2.0
2,3,7,8-TCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDD	0.1	0.25	0.5	1.0	2.0
*2,3,4,7,8-PeCDF			0.5		
*1,2,3,4,7,8-HxCDF			1.25		
1,2,3,6,7,8-HxCDF	0.25	0.625	1.25	2.5	5.0
*1,2,3,4,7,8-HxCDD			1.25		
1,2,3,6,7,8-HxCDD	0.25	0.625	1.25	2.5	5.0
*1,2,3,7,8,9-HxCDD			1.25		
*2,3,4,6,7,8-HxCDF			1.25		
*1,2,3,7,8,9-HxCDF			1.25		
*1,2,3,4,7,8,9-HpCDF			1.25		
1,2,3,4,6,7,8-HpCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,6,7,8-HpCDD	0.25	0.625	1.25	2.5	5.0
OCDD	0.5	1.25	2.5	5.0	10.0
OCDF	0.5	1.25	2.5	5.0	10.0
$^{13}C_{12}$-2,3,7,8-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-2,3,7,8-TCDF	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	1.0	1.0	1.0	1.0
$^{13}C_{12}$-OCDD	1.0	1.0	1.0	1.0	1.0
$^{13}C_{12}$-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5
$^{37}Cl_4$-2,3,7,8-TCDD			1.25		

* These compounds are only *required* in the CC3 solution. Therefore, do not perform % RSD calculations on these analytes.

Table 2
Quantitation Limits for Target Compounds

Analyte	CAS Number	Water (ng/L)	Soil (μg/kg)	Fly Ash (μg/kg)	Chemical Waste (μg/kg)
2,3,7,8-TCDD	1746-01-6	10	1.0	1.0	10
2,3,7,8-TCDF	51207-31-9	10	1.0	1.0	10
1,2,3,7,8-PeCDF	57117-41-6	25	2.5	2.5	25
1,2,3,7,8-PeCDD	40321-76-4	25	2.5	2.5	25
2,3,4,7,8-PeCDF	57117-31-4	25	2.5	2.5	25
1,2,3,4,7,8-HxCDF	70648-26-9	25	2.5	2.5	25
1,2,3,6,7,8-HxCDF	57117-44-9	25	2.5	2.5	25
1,2,3,4,7,8-HxCDD	39227-28-6	25	2.5	2.5	25
1,2,3,6,7,8-HxCDD	57653-85-7	25	2.5	2.5	25
1,2,3,7,8,9-HxCDD	19408-74-3	25	2.5	2.5	25
2,3,4,6,7,8-HxCDF	60851-34-5	25	2.5	2.5	25
1,2,3,7,8,9-HxCDF	72918-21-9	25	2.5	2.5	25
1,2,3,4,6,7,8-HpCDF	67562-39-4	25	2.5	2.5	25
1,2,3,4,6,7,8-HpCDD	35822-46-9	25	2.5	2.5	25
1,2,3,4,7,8,9-HpCDF	55673-89-7	25	2.5	2.5	25
OCDD	3268-87-9	50	5.0	5.0	50
OCDF	39001-02-0	50	5.0	5.0	50

* "Chemical waste" includes the matrices of oils, still bottoms, oily sludge, wet fuel oil, oil-laced soil, and surface water heavily contaminated with these matrices.

Table 3
Internal Standard, Recovery Standard and Cleanup Standard Solutions

Internal Standard Solution

Internal Standards	Concentration
$^{13}C_{12}$-2,3,7,8-TCDD	5 ng/µL
$^{13}C_{12}$-2,3,7,8-TCDF	5 ng/µL
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	5 ng/µL
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	10 ng/µL
$^{13}C_{12}$-OCDD	10 ng/µL

Recovery Standard Solution

Recovery Standards	Concentration
$^{13}C_{12}$-1,2,3,4-TCDD	5 ng/µL
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	5 ng/µL

Cleanup Standard Solution

Cleanup Standard	Concentration
$^{37}Cl_4$-2,3,7,8-TCDD	5 ng/µL

Table 5

Matrix Spiking Solution

Analyte	Concentration (ng/µL)
2,3,7,8-TCDD	2.5
2,3,7,8-TCDF	2.5
1,2,3,7,8-PeCDF	6.25
1,2,3,7,8-PeCDD	6.25
1,2,3,6,7,8-HxCDF	6.25
1,2,3,6,7,8-HxCDD	6.25
1,2,3,4,6,7,8-HpCDF	6.25
1,2,3,4,6,7,8-HpCDD	6.25
OCDD	12.5
OCDF	12.5

This solution is prepared in tridecane (or nonane) and diluted with acetone prior to use.

Table 6
PCDD/PCDF Isomers in the Window Defining Mix for a 60 m DB-5 Column

Homologue	First Eluted	Last Eluted	Approximate Concentration (µg/mL)
TCDD	1,3,6,8-	1,2,8,9-	1.0
TCDF	1,3,6,8-	1,2,8,9-	1.0
PeCDD	1,2,4,7,9-	1,2,3,8,9-	1.0
PeCDF	1,3,4,6,8-	1,2,3,8,9-	1.0
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-	1.0
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-	1.0
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-	1.0
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-	1.0

Table 8
Ions Specified for Selected Ion Monitoring for PCDDs/PCDFs

Analyte	Quantitation Ions		M-[COCl]+
TCDD	320	322	259
PeCDD	356	358	293
HxCDD	390	392	327
HpCDD	424	426	361
OCDD	458	460	395
TCDF	304	306	243
PeCDF	340	342	277
HxCDF	374	376	311
HpCDF	408	410	345
OCDF	442	444	379
Internal Standards			
$^{13}C_{12}$-2,3,7,8-TCDD	332	334	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	402	404	--
$^{13}C_{12}$-OCDD	470	472	--
$^{13}C_{12}$-2,3,7,8-TCDF	316	318	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	420	422	--
Recovery Standards			
$^{13}C_{12}$-2,3,7,8-TCDD	332	334	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	402	404	--
Cleanup Standard			
37Cl4-2,3,7,8-TCDD	328	(1)	265
Polychlorinated diphenyl ethers			
HxCDPE	376	--	--
HpCDPE	410	--	--
OCDPE	446	--	--
NCDPE	480	--	--
DCDPE	514	--	--

(1) There is only one quantitation ion monitored for the cleanup standard

Table 9
Criteria for Isotopic Ratio Measurements for PCDDs/PCDFs

Analyte	Selected Ions	Theoretical Ion Abundance	Control Limits
TCDD	320/322	0.77	0.65-0.89
PeCDD	356/358	1.55	1.32-1.78
HxCDD	390/392	1.24	1.05-1.43
HpCDD	424/426	1.04	0.88-1.20
OCDD	458/460	0.89	0.76-1.02
TCDF	304/306	0.77	0.65-0.89
PeCDF	340/342	1.55	1.32-1.78
HxCDF	374/376	1.24	1.05-1.43
HpCDF	408/410	1.04	0.88-1.20
OCDF	442/444	0.89	0.76-1.02
Internal Standards			
$^{13}C_{12}$-2,3,7,8-TCDD	332/334	0.77	0.65-0.89
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	402/404	1.24	1.05-1.43
$^{13}C_{12}$-OCDD	470/472	0.89	0.76-1.01
$^{13}C_{12}$-2,3,7,8-TCDF	316/318	0.77	0.65-0.89
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	420/422.	1.04	0.88-1.20
Recovery Standards			
$^{13}C_{12}$-2,3,7,8-TCDD	332/334	0.77	0.65-0.89
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	402/404	1.24	1.05-1.43

Table 10
Relationship of Internal Standards to Analytes, and Recovery Standards to Internal Standards, Cleanup Standard and Analytes

Internal Standards vs. Analytes

Internal Standard	**Analyte**
$^{13}C_{12}$-TCDD	2,3,7,8-TCDD 1,2,3,7,8-PeCDD
$^{13}C_{12}$-HxCDD	1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,7,8-HxCDD 1,2,3,4,6,7,8-HpCDD
$^{13}C_{12}$-OCDD	1,2,3,4,6,7,8,9-OCDD 1,2,3,4,6,7,8,9-OCDF
$^{13}C_{12}$-TCDF	2,3,7,8-TCDF 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF
$^{13}C_{12}$-HpCDF	1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 1,2,3,4,7,8-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,5,8,9-HpCDF 1,2,3,4,7,8,9-HpCDF

Recovery Standards vs. Analytes, Internal Standards and Cleanup Standard

Recovery Standard	**Analyte, Internal Standard**
$^{13}C_{12}$-1,2,3,4-TCDD	2,3,7,8-TCDD 1,2,3,7,8-PeCDD 2,3,7,8-TCDF 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF $^{13}C_{12}$-2,3,7,8-TCDD $^{13}C_{12}$-2,3,7,8-TCDF $^{37}Cl_4$-2,3,7,8-TCDD
13C12-1,2,3,7,8,9-HxCDD	1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 1,2,3,4,7,8-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,5,8,9-HpCDF 1,2,3,4,7,8,9-HpCDF 1,2,3,4,6,7,8,9-OCDD 1,2,3,4,6,7,8,9-OCDF $^{13}C_{12}$-1,2,3,6,7,8-HxCDD $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF $^{13}C_{12}$-OCDD

1.0 DATA COMPLETENESS FOR DIOXIN/DIBENZOFURAN ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of PCDD/PCDF data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, µg/L for waters and µg/kg for soils?

1.4 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.5 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.6 Were raw data to support analyses and QC operations present and complete?

ACTIONS: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.7 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.8 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

Criteria:

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Holding times for PCDD/PCDF:
Aqueous and solid samples – 30 days from collection to extraction, 45 days from extraction to analysis.

The holding times for extraction/preparation presented in Method 8280A are considered to be recommentdations only. PCDDs/PCDFs are very stable in a variety of matrices, and holding times under the conditions of the method may be as high as a year for certain matrices. Sample extracts are to be analyzed within 45 days of extraction.

VALIDATION ACTIONS:
If holding times for analysis of sample extracts are exceeded, positive results and detection limits are considered to be approximate (UJ, J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 INSTRUMENT PERFORMANCE (MASS CALIBRATION, GC COLUMN PEFORMANCE CHECK

Criteria:

Mass calibration
Mass calibration of the MS is recommended prior to analyzing the calibration solutions, blanks, samples and QC samples. It is recommended that the instrument be tuned to greater sensitivity in the high mass range in order to achieve better response for the later eluting compounds. Optimum results using FC-43 for mass calibration may be achieved by scanning from 222-510 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode. Under these conditions, m/z 414 and m/z 502 should be 30-50% of m/z 264 (base peak).

Was mass calibration performed at the frequency given above?

Was the criteria m/z 414 and m/z 502 should be 30-50% of m/z 264 (base peak) met?

VALIDATION ACTION:
Qualify associated positive sample results and detection limits as approximate (UJ,J).

GC Column Performance Check Solution (recommended)
On the DB-5 column,the chromatographic resolution is evaluated using the CC3 calibration standard during both the initial calibration and the calibration verification. The chromatographic peak separation between the C - 2,3,7,8-TCDD peak and the C -1,2,3,4- 13 13 12 12 TCDD peak must be resolved with a valley of 25 percent, where:
Valley = (x / y) × 100
y = the peak height of any TCDD isomer
x = measured

The resolution criteria must be evaluated using measurements made on the selected ion current profile (SICP) for the appropriate ions for each isomer. Measurements are not made from total ion current profiles. Optimize the operating conditions for sensitivity and resolution, and employ the same conditions for both calibration and sample analyses.

When an SP-2331 (or equivalent) GC column is used to confirm the results for 2,3,7,8-TCDF, the chromatographic resolution is evaluated before the analysis of any calibration standards by the analysis of a commercially-available column performance mixture that contains the TCDD isomers that elute most closely with 2,3,7,8-TCDD on this GC column (1,4,7,8-TCDD and the 1,2,3,7/1,2,3,8-TCDD pair). Analyze a 2-µL aliquot of this solution, using the column operating conditions and descriptor switching times previously established. The GC operating conditions for this column should be modified from those for the DB-5 (or equivalent) column, focusing on resolution of the closely-eluting TCDD and TCDF isomers.

The column performance mixture may be combined with the window defining mix into a single analysis, provided that the combined solution contains the isomers needed to determine that criteria for both analyses can be met.
The chromatographic peak separation between unlabeled 2,3,7,8-TCDD and the peaks representing all other unlabeled TCDD isomers should be resolved with a valley of 25%.
The resolution criteria must be evaluated using measurements made on the selected ion current profile (SICP) for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

Further analyses may not proceed until the GC resolution criteria have been met.

VALIDATION ACTION:

1 If the GC column performance check solution was not analyzed at the required frequency, qualify associated positive sample results and detection limits as approximate (UJ,J).

2 If the percent valley criteria are not met, qualify all positive data J. Do not qualify detection limits.
3.1 List below the samples qualified due to mass calibration or GC column performance excursions.

Mass resolution check ID	Excursion	Samples Affected (client/lab ID)	Action

4.0 INITIAL CALIBRATION

Criteria:

Calibration of the GC/MS system involves three separate procedures, mass calibration of the MS, establishment of GC retention time windows, and calibration of the target analytes. Samples should not be analyzed until acceptable descriptor switching times, chromatographic resolution, and calibrations are achieved and documented. The injection volume for all sample extracts, blanks, quality control samples and calibration solutions must be the same.

Retention time windows - Prior to the calibration of the target analytes, it is necessary to establish the appropriate switching times for the SIM descriptors. The switching times are determined by the analysis of the Window Defining Mix, containing the first and last eluting isomers in each homologue.

The ions in each of the four recommended descriptors are arranged so that there is overlap between the descriptors. The ions for the TCDD, TCDF, PeCDD, and PeCDF isomers are in the first descriptor, the ions for the PeCDD, PeCDF, HxCDD and HxCDF isomers are in the second descriptor, the ions for the HxCDD, HxCDF, HpCDD and HpCDF isomers are in the third, and the ions for the HpCDD, HpCDF, OCDD and OCDF isomers are in the fourth descriptor. The descriptor switching times are set such that the isomers that elute from the GC during a given retention time window will also be those isomers for which the ions are monitored. For the homologues that overlap between descriptors, the laboratory may use discretion in setting the switching times. However, do not set descriptor switching times such that a change in descriptors occurs at or near the expected retention time of any of the 2,3,7,8-substituted isomers.

Calibration of target analytes - Two types of calibration procedures, initial calibration and calibration verification, are necessary. The initial calibration is needed before any samples are analyzed for PCDDs/PCDFs, and intermittently throughout sample analysis, as dictated by the results of the calibration verification. The calibration verification is necessary at the beginning of each 12-hour time period during which sample are analyzed.

Initial Calibration - Once the Window Defining Mix has been analyzed and the descriptor switching times have been verified (and after the analysis of the column performance solution, if using a GC column other than DB-5), analyze the five concentration calibration solutions (CC1-CC5) prior to any sample analysis.

The relative ion abundance criteria for PCDDs/PCDFs should be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in all solutions. The lower and upper limits of the ion abundance ratios represent a ±15% window around the theoretical abundance ratio for each pair of selected ions. The Cl -2,3,7,8-TCDD cleanup standard contains no 35Cl, thus the ion abundance ratio criterion does not apply to this compound.

If the laboratory uses a GC column other than those described here, the laboratory must ensure that the isomers eluting closest to 2,3,7,8-TCDD on that column are used to evaluate GC column resolution

Calculate the relative response factors (RFs) for the seventeen unlabeled target analytes relative to their appropriate internal standards (RF) according to the formulae below. For the seven unlabeled analytes and the Cl -2,3,7,8- TCDD cleanup standard that are found only in the CC3 solution, only one RF is calculated for each analyte. For the other 10 unlabeled analytes, calculate the RF of each analyte in each calibration standard. Calculate the RFs for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RF) in each calibration is standard.

There is only one quantitation ion for the Cl cleanup standard. Calculate the relative response factor as described for RF , using one area for the cleanup standard, is and the sum of the areas of the ions from the recovery standard. The RFn and xRFis are dimensionless quantities; therefore, the units used to express the Qn , Qis , and Qrs must be the same.
Calculate the relative response factors for the unlabeled PCDDs/PCDFs relative to the recovery standards (RFrs)
RFrs = RFn * RFis

This relative response factor is necessary when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

Relative Response Factor Criteria - Calculate the mean RF and percent relative standard deviation (%RSD) of the five RFs (CC1 to CC5) for each unlabeled PCDD/PCDF and labeled internal standards present in all five concentration calibration solutions. No mean RF or %RSD calculations are possible for the 2,3,7,8-substituted isomers or the cleanup standard found only in the CC3 solution. The %RSD of the five RFs (CC1-CC5) for the unlabeled PCDDs/PCDFs and the internal standards should not exceed 15.0%.

VALIDATION ACTION:

1. If the %RSD for each unlabeled isomer exceeds 15, flag the associated sample positive results for that specific isomer as estimated ("J"). No effect on the non-detect data.
2. If the ion abundance ratio for an analyte is outside the limits, reject the results for that analyte (R).
3. If the ion abundance ratio for an internal or recovery standard falls outside the QC limits flag the associated positive hits with J. No effect on the non-detects.
4. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.
5. If the selected monitoring ions were not used for data acquisition, the lab must be asked for an explanation. If an incorrect ion was used, reject all the associated data.
6. If mass calibration criteria as previously described is not met, specify that in case narrative.
7. Non compliance of all other criteria specified above should be evaluated using professional judgement.

Spot check response factor calculations and ion ratios.
Ensure that the correct quantitation ions for the unlabeled PCDDs/PCDFs and internal standards were used.
Verify that the appropriate internal standard was used for each isomer.

To recalculate the response factor, use the equation:

$$RRFn = [(An^1 + An^2) \times Qis] / [(Ais^1 + Ais^2) \times Qn]$$

$$RRFis = [(Ais^1 + Ais^2) \times Qrs] / [(Ars^1 + Ars^2) \times Qis]$$

Where:

An^1 and An^2 = integrated areas of the two quantitation ions of isomer of interest.
Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.
Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.
Qn = nanograms of the unlabeled PCDD/PCDF analyte injected
Qis = nanograms of the appropriate internal standard injected
Qrs = nanograms of the appropriate recovery standard injected

4.1 List below all initial calibrations and samples qualified due to initial calibration excursions.

Unique IC ID	Excursion	Samples Affected	Action

5.0 CONTINUING CALIBRATION

Criteria:

The calibration verification consists of two parts: evaluation of the chromatographic resolution, and verification of the RF values to be used for quantitation. At the beginning of each 12-hour period, **the chromatographic resolution is verified in the same fashion as in the initial calibration**, through the analysis of the CC3 solution on the DB-5 (or equivalent) column, or through the analysis of the column performance solution on the SP-2331 (or equivalent) column. Prepare the CC3 solution by combining the volumes of the solutions to yield a final volume of 1.0 mL at the concentrations listed for the CC3 solution. Alternatively, use a commercially-prepared solution that contains the target analytes at the CC3 concentrations. For the DB-5 (or equivalent) column, begin the 12-hour period by analyzing the CC3 solution. Inject a 2-µL aliquot of the calibration verification solution (CC3) into the GC/MS. The identical GC/MS/DS conditions used for the analysis of the initial calibration solutions must be used for the calibration verification solution. Evaluate the chromatographic resolution using the QC criteria described in the instrument performance section.

For the SP-2331 (or equivalent) column, or other columns with different elution orders, begin the 12-hour period with the analysis of a 2-µL aliquot of the appropriate column performance solution. Evaluate the chromatographic resolution using the QC criteria described in the initial calibration section. If this solution meets the QC criteria, proceed with the analysis of a 2-µL aliquot of the CC3 solution. The identical GC/MS/DS conditions used for the analysis of the initial calibration solutions must be used for the calibration verification solution.

Calculate the RFs for the seventeen unlabeled target analytes relative to their appropriate internal standards (RF) and the response factors for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RF).
Calculate the RFs for the unlabeled PCDDs/PCDFs relative to the recovery standards (RF).

Do not proceed with sample analyses until the calibration verification criteria have been met for:
1) GC Column Resolution Criteria - The chromatographic resolution on the DB-5 (or equivalent) and /or the SP-2331 (or equivalent) column must meet the QC criteria described in the initial calibration section. In addition, the chromatographic peak separation between the 1,2,3,4,7,8-HxCDD and the 1,2,3,6,7,8-HxCDD in the CC3 solution shall be resolved with a valley of less than or equal to 50 percent.
2) Ion Abundance Criteria - The relative ion abundances must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards.
3) Instrument Sensitivity Criteria - For the CC3 solution, the signal-to-noise (S/N) ratio shall be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10.0 for the labeled internal and recovery standards.
4) Response Factor Criteria - The measured RFs of each analyte and internal standard in the CC3 solution must be within ±30.0% of the mean RFs established during initial calibration for the analytes in all five calibration standards, and within ±30.0% of the single-point RFs established during initial calibration for those analytes present in only the CC3 standard.

In order to demonstrate that the GC/MS system has retained adequate sensitivity during the course of sample analyses, the lowest standard from the initial calibration is analyzed at the end of each 12-hour time period during which samples are analyzed. This analysis must utilize the same injection volume and instrument operating conditions as were used for the preceding sample analyses.

The results of this analysis must meet the acceptance criteria for retention times, ion abundances, and S/N ratio for the continuing calibration standard. Response factors do not need to be evaluated in this end-of-shift standard. If this analysis fails either the ion abundance or S/N ratio criteria, then any samples analyzed during that 12-hour period that indicated the presence of any PCDDs/PCDFs below the method quantitation limit or where estimated maximum possible concentrations were reported must be reanalyzed. Samples with positive results above the method quantitation limit need not be reanalyzed.

VALIDATION ACTION:

1. If any of the requirements for retention times are not met, use professional judgement to determine the validity of the data.

2. If any requirements listed for S/N ratio and ion abundance criteria are not met reject all data (R) directly affected by each specific problem.

3. When the %D of the RRF is in between 30% and 60%, all the data for the outlier congeners are flagged (J). Data with %D above 60% are rejected (R).

4. If the continuing calibration standard was not analyzed at the required frequency, reject all the data (R). Contact Project Manager to initiate reanalysis.

5. If the resolution criteria are not met, qualify all positive data with (J). Do not qualify non-detects.

6. If the HRCC3 standard performed at the end of the 12 hour shift did not meet criteria examine the samples which were analyzed prior to this standard and use professional judgement to determine if data qualification is necessary.

7. For all other criteria, use professional judgement.

Spot check response factor calculations and ion ratios. Verify that the appropriate quantitation ions for the unlabeled PCDD/PCDFs and internal standards were used.

To calculate percent difference use the following equation:
% Difference = [(RRFi - RRFc) x 100] /[RRFi]

Where:
RRFi = Relative response factor established during initial calibration
RRFc = Relative response factor established during continuing calibration

5.1 List below all continuing calibrations and samples qualified due to continuing calibration excursions.

Unique CC ID	Compound	Excursion	Action	Samples Affected (client, lab IDs)

6.0 SAMPLE DATA (IDENTIFICATION)

Criteria:

Inject a 2-µL aliquot of the extract into the GC/MS instrument. Analyze the extract by GC/MS, and monitor all of the ions listed in the method. The same MS parameters used to analyze the calibration solutions must be used for the sample extracts.

Dilution of the sample extract is necessary if the concentration of any PCDD/PCDF in the sample has exceeded the calibration range, or the detector has been saturated. An appropriate dilution will result in the largest peak in the diluted sample falling between the mid-point and high-point of the calibration range.

Dilutions are performed using an aliquot of the original extract, of which approximately 50 µL remain from Sec. Remove an appropriate size aliquot from the vial and add it to a sufficient volume of tridecane (or nonane) in a clean 0.3-mL conical vial. Add sufficient recovery standard solution to yield a concentration of 0.5 ng/µL. Reduce the volume of the extract back down to 50 µL using a gentle stream of dry nitrogen.
The dilution factor is defined as the total volume of the sample aliquot and clean solvent divided by the volume of the sample aliquot that was diluted. Inject 2 µL of the diluted sample extract into the GC/MS, and analyze.

Diluted samples in which the MS response of any internal standard is greater than or equal to 10% of the MS response of that internal standard in the most recent calibration verification standard are quantitated using the internal standards.
Diluted samples in which the MS response of any internal standard is less than 10% of the MS response of that internal standard in the most recent calibration verification standard are quantitated using the recovery standards.

Identification Criteria
For a gas chromatographic peak to be unambiguously identified as a PCDD or PCDF, it must meet all of the following criteria.

Retention times - In order to make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time (RT) at the maximum peak height of the analyte must be within -1 to +3 seconds of the retention time of the corresponding labeled standard.
In order to make a positive identification of the 2,3,7,8-substituted isomers for which a labeled standard is *not* available, the relative retention time (RRT) of the analyte must be within 0.05 RRT units of the RRT established by the calibration verification. The RRT is calculated as follows:
For non-2,3,7,8-substituted compounds (tetra through hepta), the retention time must be within the retention time windows established by the window defining mix for the corresponding homologue.
In order to assure that retention time shifts do not adversely affect the identification of PCDDs/PCDFs, the absolute retention times of the two recovery standards added to every sample extract immediately prior to analysis may not shift by more than ±10 seconds from their retention times in the calibration verification standard.

Peak identification - All of the ions listed in the method for each PCDD/PCDF homologue and labeled standards must be present in the SICP. The ion current response for the two quantitation ions and the M-[COCL] ions for the analytes must maximize simultaneously (±2 seconds). This requirement also applies to the internal standards and recovery standards. For the cleanup standard, only one ion is monitored.

Signal-to-noise ratio - The integrated ion current for each analyte ion listed in the method must be at least 2.5 times background noise and must not have saturated the detector. The internal standard ions must be at least 10.0 times background noise and must not have saturated the detector. However, if the M-[COCL] ion does not meet the 2.5 times S/N requirement but meets all the other criteria listed previously and, in the judgement of the GC/MS Interpretation Specialist the peak is a PCDD/PCDF, the peak may be reported as positive and the data flagged on the report form.

Ion abundance ratios - The relative ion abundance criteria listed in the method for unlabeled analytes and internal standards must be met using peak areas to calculate ratios.
If interferences are present, and ion abundance ratios are not met using peak areas, but all other qualitative identification criteria are met (RT, S/N, presence of all 3 ions), then use peak heights to evaluate the ion ratio. If, in the judgement of the analyst, the peak is a PCDD/PCDF, then report the ion abundance ratios determined using peak heights, quantitate the peaks using peak heights rather than areas for both the target analyte and the internal standard, and flag the result on the report form.

Polychlorinated diphenyl ether (PCDPE) interferences. -The identification of a GC peak as a PCDF cannot be made if a signal having S/N greater than 2.5 is detected at the same retention time (±2 seconds) in the corresponding PCDPE channel. If a PCDPE is detected, an Estimated Maximum Possible Concentration (EMPC) should be calculated for this GC peak regardless of the ion abundance ratio, and reported.
When peaks are present that do not meet all of the identification criteria and the reporting of an estimated maximum possible concentration will not meet the specific project objectives, then the analyst may need to take additional steps to resolve the potential interference problems. However, this decision generally is project-specific and should not be applied without knowledge of the intended application of the results. These steps may be most appropriate when historical data indicate that 2,3,7,8-substituted PCDDs/PCDFs have been detected in samples from the site or facility, yet the results from a specific analysis are inconclusive.

For solid matrices, the units of ng/g that result from the formula above are equivalent to µg/kg. Using isotope dilution techniques for quantitation the concentration data are recovery corrected, and therefore, the volume of the final extract and the injection volume are implicit in the value of Qis.

For homologues that contain only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the RF of the 2,3,7,8-substituted isomer from the calibration verification will be used to quantitate both the 2,3,7,8-substituted isomers and the non-2,3,7,8-isomers.
For homologues that contain *more than* one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF, and HpCDF), the RF used to calculate the concentration of each 2,3,7,8-substituted isomers will be the RF determined for that isomer during the calibration verification.
For homologues that contain one or more non-2,3,7,8-substituted isomer, the RF used to calculate the concentration of these isomers will be the lowest of the RFs determined during the calibration verification for the 2,3,7,8-substituted isomers in that homologue. This RF will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.

The relative response factors of given isomers within any homologue may be different. However, for the purposes of these calculations, it will be assumed that every non-2,3,7,8-substituted isomer for a given homologue has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, the 2,3,7,8-substituted isomer with the lowest RF was chosen as representative of each homologue. All relative response factor calculations for the non-2,3,7,8-substituted isomers in a given homologue are based on that isomer.

In addition to the concentrations of specific isomers, the total homologue concentrations are also reported. Calculate the total concentration of each homologue of PCDDs/PCDFs as follows:
Total concentration = sum of the concentrations of every positively identified isomer of each PCDD/PCDF homologue.
The total must include the non-2,3,7,8-substituted isomers as well as the 2,3,7,8-substituted isomers that are also reported separately. The total number of GC peaks included in the total homologue concentration should be reported.

If the area of any internal standard in a diluted sample is less than 10% of the area of that internal standard in the calibration verification standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the recovery standard instead of the internal standard. The purpose is to ensure that there is an adequate MS response for quantitation in a diluted sample. While use of a smaller aliquot of the sample might require smaller dilutions and therefore yield a larger area for the internal standard in the diluted extract, this practice leads to other concerns about the homogeneity of the sample and the representativeness of the aliquot taken for extraction.

VALIDATION ACTION:

1. Reject (R) all positive data for the analytes which do not meet criteria for retention times for 2378 substituted isomers and non-2378 substituted isomers, and the presence of all ions for each isomer and labeled standards in the SICP.

2. If the criteria for the integrated ion current for each ion for the analytes being 2.5 times the background noise are not met but all other criteria are met, qualify all positive data of the specific analyte with J.

3. If the requirements for the integrated ion current for the internal ions being 10 times the background noise are not met but all other requirements are met qualify the positive data of the corresponding analytes as approximate (J).

4. If the analytes reported positive do not meet ion abundance criteria for analytes, reject (R) all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).

5. If the internal standards and recovery standards do not meet ion abundance criteria but they meet all other criteria flag all corresponding data with "J".

6. If PCDF is detected but an interfering PCDPE is also detected reject the PCDF data (R). The reported value of PCDF is changed to EMPC.

7. If the lab did not monitor for PCDPEs, qualify all positive furan data as approximate (J).

Spot check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate concentration and EMPC. Ensure that the proper PCDDs/PCDFs and internal standards were used.

To recalculate the concentration of individual PCDD/PCDF isomers in the sample use the following equation:

Non-Aqueous Matrices:

$$Cn\ (\mu g/kg) = [Qis \times (An1 + An2)]/[W \times (Ais1 + Ais2) \times RRFn]$$

WATER

$$Cn\ (ng/L) = [Qis \times (An^1 + An^2)]/[V \times (Ais^1 + Ais^2) \times RRFn]$$

Where:

An^1 and An^2 = integrated ion abundances (peak areas) of the quantitation ions of the isomer of interest.

Ais^1 and Ais^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard.

W= Weight (g) of sample extracted

V= Volume (L) of sample extracted

Qis= Quantity (ng) of the appropriate internal standard added to the sample prior to extraction

RFn= Calculated relative response factor from continuing calibration.

6.1 List samples qualified due to identification excursions.

Sample ID (client/lab)	**Compound**	**Excursion**	**Action**

7.0 ESTIMATED DETECTION LIMITS (EDL)

Criteria:
The sample specific estimated detection limit (EDL) is the estimate made by the laboratory of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The estimate is specific to a particular analysis of the sample, and will be affected by sample size, dilution, etc.
An EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for 2,3,7,8-substituted isomers giving responses for both the quantitation ions that are less than 2.5 times the background level.
Use the formulae below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level (H) is determined by measuring the height of the noise at the expected retention times of both the quantitation ions of the particular 2,3,7,8-substituted isomer.

Use the equation below to check EDL calculations:

Non-Aqueous Matrices
$$EDL\ (\mu g/kg) = [2.5 \times Qis \times (Hx^1 + Hx^2) \times D]/[W \times (His^1 + His^2) \times RFn]$$

WATER
$$EDL\ (ng/L) = [2.5 \times Qis \times (Hx^1 + Hx^2) \times D]/[V \times (His^1 + His^2) \times RRFn]$$

Where:
Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.
His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.
D = dilution factor
Where:
W= Weight (g) of sample extracted
V= Volume (ml) of sample extracted
Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction
RRFn= Calculated relative response factor from continuing calibration.

VALIDATION ACTION:
Check the EDL data to verify calculation.

8.0 ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC)

Criteria:

An estimated maximum possible concentration (EMPC) is calculated for 2,3,7,8-substituted isomers that are characterized by a response with an S/N of at least 2.5 for both the quantitation ions, and meet all of the identification criteria except the ion abundance ratio criteria or when a peak representing a PCDPE has been detected. An EMPC is a worst-case estimate of the concentration.

Use the equation below to check EMPC calculations:

Nonaqueous Matrices

EMPC (µg/kg) = $[(Ax^1 + Ax^2) \times Qis \times D]/[(Ais^1 + Ais^2) \times RFn \times W]$

WATER

EMPC (ng/L) = $[(Ax^1 + Ax^2) \times Qis \times D]/[(Ais^1 + Ais^2) \times RFn \times V]$

Where:

Ax1 and Ax2 = areas of both quantitation ions.

Ais^1 and Ais^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard.

W= Weight (g) of sample extracted

V= Volume (ml) of sample extracted

Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction

RRFn= Calculated relative response factor from continuing calibration.

D is dilution factor.

VALIDATION ACTIONS:

1. If EDL or EMPC of an analyte which was not reported as present is missing, contact the laboratory for correction.

2. If the spot check calculations yielded EDLs or EMPCs different from those reported in Form I, contact the laboratory for an explanation.

Check EMPC calculation.

9.0 BLANK ANALYSIS (METHOD, RINSATE, FIELD)

Method Blank

Criteria:
Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?

If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event?

VALIDATION ACTION:
1. If the proper number of method blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the method blank is contaminated with any of the isomers at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

Rinsate Blank

Criteria:

One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent. Was rinsate blanks collected at the above frequency?

VALIDATION ACTION:
1. If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the Project Manager to discuss what proper action must be taken.

Field Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

Criteria:

The field blanks are blind blanks at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

9.1 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

10.0 INTERNAL STANDARDS EVALUATION

Criteria:
If the area of any internal standard in a diluted sample is less than 10% of the area of that internal standard in the calibration verification standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the recovery standard instead of the internal standard. The purpose is to ensure that there is an adequate MS response for quantitation in a diluted sample. While use of a smaller aliquot of the sample might require smaller dilutions and therefore yield a larger area for the internal standard in the diluted extract, this practice leads to other concerns about the homogeneity of the sample and the representativeness of the aliquot taken for extraction.

When calculating the recovery of the 37Cl4 -2,3,7,8-TCDD cleanup standard, only one m/z is monitored for this standard; therefore, only one peak area will be used in the numerator of this formula. Use both peak areas of the 12C12 1,2,3,4-TCDD recovery standard in the denominator.

The C -1,2,3,4-TCDD is used to quantitate the TCDD and TCDF internal standards and the cleanup standard, and the C -1,2,3,7,8,9-HxCDD is used to quantitate the HxCDD, HpCDF and OCDD internal standards.

If the original sample, prior to any dilutions, has any internal standard with a percent recovery of less than 25% or greater than 150%, re-extraction and reanalysis of that sample is necessary.

VALIDATION ACTION:

1. If the internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.
2. If the internal standard recovery is above the upper limit (150 percent) flag all associated data (positive and non-detect data) with "J".
3. If the internal standard recovery is less than 10%, qualify all associated data reject (R) when highly toxic isomers (TEF> 0.05) are affected, notify Project Manager to initiate re-collection.

Recalculate the percent recovery for internal standards in the sample extract, Ris, using the formula:

$$Ris = [(Ais^1 + Ais^2) \times Qrs \times 100\%] / [(Ars^1 + Ars^2) \times RRFis \times Qis]$$

Where:
Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.
Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.
Qis = quantity of the appropriate internal standard injected (pg)
Qrs = quantity of the appropriate recovery standard injected (pg)
RRFn= Calculated relative response factor from continuing calibration.

10.1 List samples qualified due to internal standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Action

11.0 RECOVERY STANDARDS

Criteria:
There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration?
Area upper limit= +100% of recovery standard area.
Area lower limit= -50% of recovery standard area.

When calculating the recovery of the 37Cl4 -2,3,7,8-TCDD cleanup standard, only one m/z is monitored for this standard; therefore, only one peak area will be used in the numerator of this formula. Use both peak areas of the 12C12 1,2,3,4-TCDD recovery standard in the denominator.

The C -1,2,3,4-TCDD is used to quantitate the TCDD and TCDF internal standards and the cleanup standard, and the C -1,2,3,7,8,9-HxCDD is used to quantitate the HxCDD, HpCDF and OCDD internal standards.

Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?

VALIDATION ACTION:

1. If the recovery standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, reject all associated non-detect data (R) and flag the positive data (J).

3. If the retention time of the recovery standard differs by more than 10 seconds from the daily calibration use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the GC column performance check solution.

11.1 List samples qualified due to recovery standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Recovery Standard	Area and Percent Recovery	Action

12.0 MATRIX SPIKE

Criteria:
Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?

.2 Was the percent recovery of the analytes within laboratory control limits?

VALIDATION ACTIONS:
The control limits of the matrix spike data are used to flag data of the unspiked sample only; flag analytes as approximated (UJ,J) if control limits are exceeded.

12.1 List samples qualified due to matrix spike excursions.

INSTRUMENT:

Matrix Spike ID	**Analyte**	**Excursion**	**Samples Affected (client/lab ID)**	**Action**

13.0 DUPLICATE SAMPLES

Criteria:
Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency?

Did results of the duplicate samples meet laboratory control limits?

VALIDATION ACTION:
Qualify the original sample as approximate (UJ,J) if control limits are exceeded.

13.1 List samples qualified due to duplicate excursions.

Instrument:

Duplicate ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

14.0 SECOND COLUMN CONFIRMATION

Criteria:
The sample extract may be reanalyzed on a 60 m SP-2330 or SP-2331 GC column (or equivalent) in order to achieve better GC resolution, and therefore, better identification and quantitation of 2,3,7,8-TCDF. Other columns that provide better specificity for 2,3,7,8-TCDF than the DB-5 column may also be used. Regardless of the GC column used, for a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF isomer during the second column confirmation, it must meet the ion abundance, signal-to-noise, and retention time criteria.

The second column confirmation analysis may be optimized for the analysis of 2,3,7,8-TCDF, and need not be used to confirm the results for any other 2,3,7,8-substituted PCDDs/PCDFs identified during the original analysis.

VALIDATION ACTIONS:
If confirmation is missing, use professional judgement, or contact Project Manager for assistance.

1 Did the second column meet the initial calibration and continuing calibration specifications as previously described?

14.1 List samples affected by second column confirmation excursions.

Instrument:

Sample ID (client/lab ID)	Analyte	Excursion	Action

15.0 SAMPLE REANALYSIS

Criteria:

Due to a variety of situations that may occur during sample analysis the laboratory is required to reanalyze or reextract and reanalyze certain samples.

VALIDATION ACTIONS:
If a reanalysis was required but was not performed, contact Project Manager to initiate reanalysis. List below all reextractions and reanalyses and identify the PCDD/PCDF sample data summaries which must be used by the data user (when more than one is submitted).

15.1 List samples affected by sample reanalysis excursions.

Instrument:

Sample ID (client/lab)	Analyte	Excursion	Action

16.0 TOXICITY EQUIVALENCY FACTOR (TEF)

Criteria:

Toxic equivalent concentration (TEQ) calculation - The 2,3,7,8-TCDD toxic equivalent concentration of PCDDs/PCDFs present in the sample is calculated according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Centers for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the seventeen 2,3,7,8-substituted PCDDs/PCDFs *("Update of Toxicity Equivalency Factors [TEFs] for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and -Dibenzofurans [CDDs/CDFs]" March 1989 [EPA 625/3-89/016]).*

The 2,3,7,8-TCDD TEQ of the PCDDs/PCDFs present in the sample is calculated by summing the product of the concentration for each of the compounds and the TEF for each compound. The principal purpose of making this calculation is to provide the data user with a single value, normalized to the toxicity of 2,3,7,8-TCDD, that can more readily be used in decisions related to mixtures of these highly toxic compounds.

The exclusion of homologues such as mono-, di-, tri- and the non-2,3,7,8-substituted isomers in the higher homologues does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less than the toxicity of the compounds. Hence, only the 2,3,7,8-substituted isomers are included in the TEF calculations. The procedure for calculating the 2,3,7,8-TCDD toxic equivalence cited above is not claimed by the CDWG to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "consensus recommendation on science policy."

When calculating the TEQ of a sample, include only those 2,3,7,8-substituted isomers that were detected in the sample and met all of the qualitative identification criteria. Do not include EMPC or EDL values in the TEQ calculation.
The TEQ of a sample is also used in this analytical procedure to determine when second column confirmation may be necessary. The need for second column confirmation is based on the known difficulties in separating 2,3,7,8-TCDF from other isomers. Historical problems have been associated with the separation of 2,3,7,8-TCDF from 1,2,4,9-, 1,2,7,9-, 2,3,4,6-, 2,3,4,7- and 2,3,4,8-TCDF. Because of the toxicological concern associated with 2,3,7,8-TCDF, additional analyses may be required for some samples as described below. If project-specific requirements do not include second column confimation or specify a different approach to confirmation, then this step may be omitted and the project-specific requirements take precedence.

If the TEQ calculated is greater than 0.7 ppb for soil/sediment or fly ash, 7 ppb for chemical waste, or 7 ppt for an aqueous sample, and 2,3,7,8-TCDF is either detected or reported as an EMPC,then better isomer specificity may be required than can be achieved on the DB-5 column. The TEQ values listed here for the various matrices are equivalent to 70% of the historical "Action Level" set by the CDC for soil concentrations of 2,3,7,8-TCDD at Superfund sites. As such, it provides a conservative mechanism for determining when the additional specificity provided by a second column confirmation may be required.

The sample extract may be reanalyzed on a 60 m SP-2330 or SP-2331 GC column (or equivalent) in order to achieve better GC resolution, and therefore, better identification and quantitation of 2,3,7,8-TCDF. Other columns that provide better specificity for 2,3,7,8-TCDF than the DB-5 column may also be used.

Regardless of the GC column used, for a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF isomer during the second column confirmation, it must meet the ion abundance, signal-to-noise, and retention time criteria.

The second column confirmation analysis may be optimized for the analysis of 2,3,7,8-TCDF, and need not be used to confirm the results for any other 2,3,7,8-substituted PCDDs/PCDFs identified during the original analysis.

VALIDATION ACTION:
1. If the toxicity equivalency calculations were not performed properly notify Project Manager.

2. If the toxicity equivalency exceeded the required limits (0.7 ppb for soil/sediment, 7ppt for aqueous and 7ppb for chemical waste samples), and the lab failed to reanalyze the samples on a specific secondary column, notify the Project Manager.

16.1 List samples affected by TEF excursions.

INSTRUMENT:

Sample ID	Analyte	Excursion	Action

17.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

17.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form

USEPA Method 8280A Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS (High Resolution GC/Low Resolution MS)

Date:____________________ Number of samples and compounds per sample:_______________

Project Number:____

Validator:____Equipment Blanks:________

Project: ____Blind/Field Duplicates:______

Laboratory:____MS/MSDs:_______________

QAPP:____ DV Guidelines: USEPA Region II

Laboratory package number:____________________PARTIAL VALIDATION

Method reference:

- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd Edition. Washington D.C.*

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8280A	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method 8280A	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms

Method 8280A Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS

The following worksheets are based on:

- USEPA. 1994 *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS),* Albany, New York. (Edited for 8280A)
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd Edition. Washington D.C.*

Table of Contents:

VALIDATION DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the qualifiers assigned to results in the data validation process.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

U - Not detected above the reported detection limit.

NJ - There is presumptive evidence for the presence of the compound at an estimated value.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is not reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR DIOXIN/DIBENZOFURAN ANALYSIS

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues with sample receipt or condition of samples.

1.2 Were sample results for each parameter corrected for percent solids for soil samples?
ACTION: If any sample analyzed as a soil, other than TCLP, contains 50%-90% water, all data should be flagged as estimated (J). If a soil sample other than TCLP contains more than 90% water, all data should be qualified as unusable (R).

1.3 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.4 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.5 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

Criteria:

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Holding times for PCDD/PCDF:
Aqueous and solid samples – 30 days from collection to extraction, 45 days from extraction to analysis.

The holding times for extraction/preparation presented in Method 8280A are considered to be recommendations only. PCDDs/PCDFs are very stable in a variety of matrices, and holding times under the conditions of the method may be as high as a year for certain matrices. Sample extracts are to be analyzed within 45 days of extraction.

VALIDATION ACTION:
If holding times for analysis of sample extracts are exceeded, positive results and detection limits are considered to be approximate (UJ, J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 BLANK ANALYSIS (METHOD, RINSATE, FIELD)

Method Blank

Criteria:
Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?

If samples of some matrix were analyzed in different events (i.e. different shifts or days) has one blank for each matrix been extracted and analyzed for each event?

VALIDATION ACTION:
1. If the proper number of method blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the method blank is contaminated with any of the isomers at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

Rinsate Blank

Criteria:

One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent. Was rinsate blanks collected at the above frequency?

VALIDATION ACTION:
1. If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the Project Manager to discuss what proper action must be taken.

Field Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

Criteria:

The field blanks are blind blanks at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

3.1 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

4.0 INTERNAL STANDARDS EVALUATION

Criteria:
If the area of any internal standard in a diluted sample is less than 10% of the area of that internal standard in the calibration verification standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the recovery standard instead of the internal standard. The purpose is to ensure that there is an adequate MS response for quantitation in a diluted sample. While use of a smaller aliquot of the sample might require smaller dilutions and therefore yield a larger area for the internal standard in the diluted extract, this practice leads to other concerns about the homogeneity of the sample and the representativeness of the aliquot taken for extraction.

VALIDATION ACTION:

1. If the internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.
2. If the internal standard recovery is above the upper limit (150 percent) flag all associated data (positive and non-detect data) with "J".
3. If the internal standard recovery is less than 10%, qualify all associated data reject (R) when highly toxic isomers (TEF> 0.05) are affected, notify Project Manager to initiate re-collection.

4.1 List samples qualified due to internal standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	**Internal Standard**	**Area and Percent Recovery**	**Action**

5.0 RECOVERY STANDARDS

Note: for partial validation, evaluate if recovery forms are provided by the laboratory.

Criteria:

There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration?
Area upper limit= +100% of recovery standard area.
Area lower limit= -50% of recovery standard area.

When calculating the recovery of the 37Cl4 -2,3,7,8-TCDD cleanup standard, only one m/z is monitored for this standard; therefore, only one peak area will be used in the numerator of this formula. Use both peak areas of the 12C12 1,2,3,4-TCDD recovery standard in the denominator.

The C -1,2,3,4-TCDD is used to quantitate the TCDD and TCDF internal standards and the cleanup standard, and the C -1,2,3,7,8,9-HxCDD is used to quantitate the HxCDD, HpCDF and OCDD internal standards.

Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?

VALIDATION ACTION:

1. If the recovery standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, reject all associated non-detect data (R) and flag the positive data (J).

5.1 List samples qualified due to recovery standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Recovery Standard	Area and Percent Recovery	Action

6.0 MATRIX SPIKE

Criteria:
Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

6.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?

6.2 Was the percent recovery of the analytes within laboratory control limits?

VALIDATION ACTIONS:
The control limits of the matrix spike data are used to flag data of the unspiked sample only; flag compounds as approximate (UJ,J) if control limits are exceeded.

List samples qualified due to matrix spike excursions.

INSTRUMENT:

Matrix Spike ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

7.0 DUPLICATE SAMPLES

Criteria:
Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency?

Did results of the duplicate samples meet laboratory control limits?

VALIDATION ACTION:
Sample results for the original sample; flag compounds as approximate (UJ,J) if control limits are exceeded.

7.1 List samples qualified due to duplicate excursions.

INSTRUMENT:

Duplicate ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

Section 10

O'Brien & Gere Engineers. Inc. Data Validation Form – USEPA Method TO-17 (8260B) Volatile Organics in Air – Full Validation

O'Brien & Gere Engineers. Inc. Data Validation Form – USEPA Method TO-17 (8260B) Volatile Organics in Air – Partial Validation

SECTION 10

O'Brien & Gere Engineers Data Validation Form
USEPA Method TO-17 (8260B) Volatile Organics In Air
Date:____________________ **Number of samples and compounds per sample:**______________
Project Number:____ **Trip Blanks:**____________
Validator:____ **Equipment Blanks:**________
Project: ____ **Blind/Field Duplicates:**_____
Laboratory:____ **MS/MSDs:**______________
QAPP:_______________________________ **DV Guidelines: USEPA Region V**
Laboratory package number:_________________ **FULL VALIDATION**
Method reference:

- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes,* Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition*. Washington, D.C.

CT	Sample, EB, MS/MSD, FD Identification	Date collected 1999 2000	Date received 1999 2000	Method TO17	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number
MS/MSD indicates matrix spike/matrix spike duplicate

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
For Analyses of Volatile Organics by USEPA Method TO-17 (Air)

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data.* Chicago, Illinois
- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes.* Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review.* EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846),* 3rd Edition. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA Method TO-17. (Region V guidelines apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

USEPA Method TO-17 Information

This method describes a sorbent tube/thermal desorption/gas chromatographic-based monitoring method for volatile organic compounds (VOCs) in ambient air at 0.5 to 25 parts per billion (ppbv) concentration levels. Performance criteria are provided as part of the method in Section 14. EPA has previously published Compendium Method TO-1 describing the use of the porous polymer Tenax® GC for sampling nonpolar VOCs and Compendium Method TO-2 describing the use of carbon molecular sieve for highly volatile, nonpolar organics (1). Since these methods were developed, a new generation of thermal desorption systems as well as new types of solid adsorbents have become available commercially. These sorbents are used singly or in multisorbent packings. Tubes with more than one sorbent, packed in order of increasing sorbent strength are used to facilitate quantitative retention and desorption of VOCs over a wide volatility range. The higher molecular weight compounds are retained on the front, least retentive sorbent; the more volatile compounds are retained farther into the packing on a stronger adsorbent. The higher molecular weight compounds never encounter the stronger adsorbents, thereby improving the efficiency of the thermal desorption process.

The analytical approach using gas chromatography/mass spectroscopy (GC/MS) is identical to that mentioned in Compendium Method TO-15 and, as noted later, is adapted for this method once the sample has been thermally desorbed from the adsorption tube onto the focusing trap of the analytical system.

Summary of Method

The monitoring procedure involves pulling a volume of air through a sorbent packing to collect VOCs followed by a thermal desorption-capillary GC/MS analytical procedure.

Key steps of this method are listed below.

Selection of a sorbent or sorbent mix tailored for a target compound list, data quality objectives and sampling environment.
Screening the sampling location for VOCs by taking single tube samples to allow estimates of the nature and amount of sample gases.
Initial sampling sequences with two tubes at nominally 1 and 4 liter total sample volumes (or appropriate proportional scaling of these volumes to fit the target list and monitoring objectives).
Analysis of the samples and comparison to performance criteria.
Acceptance or rejection of the data.
If rejection, then review of the experimental arrangement including repeat analysis or repeat analysis with backup tubes and/or other QC features.
[Note: EPA requires the use of distributed volume pairs or monitoring to insure high quality data. However, in situations where acceptable data have been routinely obtained through use of distributed volume pairs and the ambient air is considered well characterized, cost considerations may warrant single tube sampling. Any attendant risk to data quality objectives is the responsibility of the project's decision maker.]

Key steps in sample analysis are listed below.

Dry purge of the sorbent tube with dry, inert gas before analysis to remove water vapor and air. The sorbent tube can be held at temperatures above ambient for the dry purge.
Thermal desorption of the sorbent tube (primary desorption).
Analyte refocusing on a secondary trap.
Rapid desorption of the trap and injection/transfer of target analytes into the gas chromatograph (secondary desorption).
Separation of compounds by high resolution capillary gas chromatography (GC).
Measurement by mass spectrometry (MS) or conventional GC detectors (only the MS approach is explicitly referred to in Compendium Method TO-17; an FID/ECD detector combination or other GC detector can be used if Section 14 criteria are met. However, no explicit QA guidelines are given here for those alternatives).

Using previously prepared identification and quantification subroutines, identify the target compounds and document the amount of each measured compound. Compare the results of analysis for the distributed volume pair taken during each sampling run and use the comparison to determine whether or not the performance criteria for individual sampling events have been met. Also examine the results of any laboratory blanks, field blanks, and any backup tube being used. Accept or reject the data based on the performance criteria.

The target compound list (TCL) is the same as listed in Compendium Method TO-15 (i.e., subsets of the 97 VOCs listed as hazardous pollutants in Title III of the Clean Air Act Amendments of 1990). Only a portion of these compounds has been monitored by the use of solid adsorbents. This method provides performance criteria to demonstrate acceptable performance of the method (or modifications of the method) for monitoring a given compound or set of compounds.

Significance

This method is an alternative to the canister-based sampling and analysis methods that are presented in Compendium Methods TO-14 and TO-15 and to the previous sorbent-based methods that were formalized as Compendium Methods TO-1 and TO-2. All of these methods are of the type that include sampling at one location, storage and transport of the sample, and analysis at another, typically more favorable site.

In keeping with the consensus of EPA scientists and science advisors, the method is performance-based such that performance criteria are provided. Any modification of the sorbent approach to monitoring for VOCs can be used provided these criteria are met.

Tube and Sorbent
Select a tube and sorbent packing for the sampling.
Condition newly packed tubes for at least 2 hours (30 min for preconditioned, purchased tubes) at 350EC while passing at least 50 mL/min of pure helium carrier gas through them.
Once conditioned, seal the tube with brass, 1/4 inch Swagelok® -type fittings and PTFE ferrules. Wrap the sealed tubes in uncoated aluminum foil and place the tubes in a clean, airtight, opaque container.
Store in a refrigerator (organic solvent-free) at 4EC if not to be used within a day. On second and subsequent uses, the tubes will generally not require further conditioning as above. However, tubes with an immediate prior use indicating high levels of pollutant trace gases should be reconditioned prior to continued usage.
Select sampling rates compatible with the collection of 1 and 4 liter total sample volume (or of proportionally lower/higher sampling volumes).
Air samples are collected over 1 hour with a sampling rate of 16.7 mL/min and 66.7 mL/min, respectively.
At the monitoring location, keep the tubes in their storage and transportation container to equilibrate with ambient temperature.
Using clean gloves, remove the sample tubes from the container, take off their caps and attach them to the sampling lines with non-outgassing flexible tubing. Uncap and immediately reseal the required number of field blank tubes.
Place the field blank tubes back in the storage container. If back-up tubes are being used, attach them to the sampling tubes using clean, metal Swagelok® type unions and combined PTFE ferrules.
Sample over the selected sampling period (i.e., 1-hour).
Immediately remove the sampling tubes with clean gloves, recap the tubes with Swagelok® fittings using PTFE ferrules, rewrap the tubes with uncoated Al foil, and place the tubes in a clean, opaque, airtight container.
If not to be analyzed during the same day, place the container in a clean, cool (<4EC), organic solvent-free environment and leave there until time for analysis.

Dry Purge the Tubes and Prepare for Thermal Desorption
Remove the sampling tubes, any backup tubes being used, and blanks from the storage area and allow the tubes to come to room temperature. Using clean gloves, remove the Swagelok®-type fittings and dry purge the tubes with a forward (sampling direction) flow of, for example, 50 mL/min of dry helium for 4 minutes.
[Note: Do not dry purge the laboratory blanks.]
Reseal the tubes with Teflon® (or other) caps compatible with the thermal desorber operation. Place the sealed tubes on the thermal desorber (e.g., Perkin Elmer Model ATD 400 Automated System or equivalent). Other thermal desorbers may have different arrangements for automation. Alternatively, use equivalent manual desorption.
Repurge of Tube on the Thermal Desorber/Addition of Internal Standard
Because of tube handling after dry purge, it may be necessary to repurge each of the tubes with pure, dry helium (He) before analysis in order to eliminate any oxygen.
If the initial dry purge can be performed on the thermal desorber so as to prevent any further exposure of the sorbent to air, then this step is not necessary. Proceed with the addition of an internal standard to the sorbent tube or the focusing tube.

Thermally Desorb the Packing
Reverse the flow direction of He gas, set the flow rate to at least 30 mL/min, and heat the tube to 325EC (in this case) to achieve a transfer of VOCs onto a focusing tube at a temperature of 27EC. Thermal desorption continues until all target species are transferred to the focusing trap. The focusing trap is typically packed with 20 mg of Carbopack™ B (60/80 mesh) and 50 mg of a Carboxen™ 1000-type sorbent (60/80 mesh).

Trap Desorption and GC/MS Analysis
After each tube is desorbed, rapidly heat the focusing trap (to 325EC in this example) and apply a reverse flow of at least 3 mL/min of pure helium carrier gas. Sample splitting is necessary to accommodate the capillary column. Analytes are transferred to the column in a narrow band of vapor.
The GC run is initiated based on a time delay after the start of thermal desorption. The remaining part of the analytical cycle is described in Section 3 of Compendium Method TO-15.

Minimizing Artifact Interference.
Stringent tube conditioning and careful tube capping and storage procedures are essential for minimizing artifacts.

Minimizing Interference from Water
There are three preferred approaches to reducing water interference during air monitoring using sorbent tubes. The first is to minimize

water collection by selecting, where possible, a hydrophobic sorbent for the sample tube.
If the sample loading is high, it is usually possible to eliminate sufficient water to prevent analytical interference by using sample splitting.
The third water management method is to dry purge either the sorbent tube itself or the focusing trap or both. Dry purging the sample tube or focusing trap simply involves passing a volume of pure, dry, inert gas through the tube from the sampling end, prior to analysis.

Detection Limits and Maximum Quantifiable Concentrations of Air Pollutants
Detection limits for atmospheric monitoring vary depending on several key factors. They are:
- Minimum artifact levels.
- GC detector selection.
- Volume of air sampled. The volume of air sampled is in turn dependent upon a series of variables including SSVs, pump flow rate limitations and time-weighted-average monitoring time constraints.

Generally speaking, detection limits range from sub-part-per-trillion (sub-ppt) for halogenated species such as CCl4 and the freons using an electron capture detector (ECD) to sub-ppb for volatile hydrocarbons in 1 L air samples using the GC/MS operated in the full SCAN mode.
Detection limits are greatly dependent upon the proper management of water for GC capillary analysis of volatile organics in air using sorbent technology.

Sampling Procedure Verification - Use of Blanks, Distributed Volume Pairs, Back-Up Tubes, and Distributed Volume Sets
Field and Laboratory Blanks
Laboratory blanks must be identically packed tubes, from the same batch, with similar history and conditioned at the same time as the tubes used for sample collection. At least two are required per monitoring exercise. They must be stored in the laboratory in clean controlled conditions (<4°C) throughout the monitoring program and analyzed at the same time as the samples-- one at the beginning and one at the end of the sequence of runs.
Field blanks are the same as laboratory blanks except that they are transported to and from the monitoring site, are uncapped and immediately resealed at the monitoring site, but do not actually have air pumped through them. One field blank tube is taken for every ten sampled tubes on a monitoring exercise and no less than two field blanks should be collected, however small the monitoring study. The field blanks should be distributed evenly throughout the set of sampled tubes to be analyzed.

Distributed Volume Pairs
When monitoring for specific analytes using a validated sorbent tube but in an uncharacterized atmosphere, it is advisable to collect distributed volume tube pairs - e.g. 1 and 4 L samples - in parallel at every monitoring location as described in Section 6. If single tube sampling is used to reduce analysis costs, a reduction in the quality assurance associated with this method has to be assumed.

Back-up tubes (identical to those used for sample collection) should be used to investigate situations in which distributed volume pairs do not agree within acceptable tolerance. To use back-up tubes, a second identical sampling tube is placed in series with a primary (front) tube. The purpose of the backup tube is to capture compounds that pass through the primary tube because of breakthrough. Analysis of the backup tube may indicate unexpected breakthrough or give evidence of channeling of sample through the tube because of loose packing.

Sample Storage
Samples should be refrigerated at <4°C in a clean environment during storage and analyzed within 30 days of sample collection (within one week for limonene, carene, bis-chloromethyl ether and labile sulfur or nitrogen-containing volatiles). Samples taken on tubes containing multiple sorbent beds should be analyzed as soon as possible after sampling unless it is know in advance that storage will not cause significant sample recovery errors.

The calibration procedure becomes identical to that presented in Section 3 of Compendium Method TO-15. The guidance given in Section 3 of Compendium Method TO-15 concerning multi-level calibration procedures and calibration frequencies should be followed for this Compendium method. It is also advisable to analyze a single level calibrant (i.e. tubes loaded with analyte masses in the mid-range of those expected to be collected during sampling) approximately every tenth sample during an analytical sequence, as a check on system performance. All samples processed that exceed the calibration range will require data qualifiers to be attached to the analytical results.

Blanks
Artifact levels on laboratory and field blanks should be at the low or sub-nanogram level for carbonaceous sorbents and Tenax® and at the double digit ng level for Porapaks®, Chromosorb® Century series sorbents and other porous polymers. If artifact levels are considerably above this, careful attention must be paid to the tube conditioning and storage procedures .

Artifact peaks which are 10% or more of the area of average component peaks should be marked as artifacts in the final data reports. When monitoring unknown atmospheres, special care must be taken to distinguish between sorbent artifacts and analytes, using the MS to identify components which are significant in both blank and sampled tubes.
If the same profile/pattern of VOCs is observed on the field blanks as on the sampled tubes and if the level of these components is 5% or more of the sampled volatiles, careful attention must be paid to the method of sealing the tubes and other storage procedures in future studies. If the profile of volatiles on the field blanks matches that of the sampled tubes and if the areas of the peaks on the field blank are

10% or more of sampled tube levels, the sampled tube data are invalidated.

Performance Criteria for the Solid Adsorbent Sampling of Ambient Air

There are four performance criteria which must be met for a system to qualify under Compendium Method TO-17. These criteria are:

- A method detection limit #0.5 ppb.
- Duplicate (analytical) precision within 20% on synthetic samples of a given target gas or vapor in a typical target gas or vapor mix in humidified zero air.
- Agreement within 25% for distributed volume pairs of tubes taken in each sampling set.
- Audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppb). Either mass spectrometry as emphasized here, or specific detectors can be used for analysis.

Method Detection Limit

The method detection limit is defined for each system by making seven replicate measurements of a concentration of the compound of interest near the expected detection limit (within a factor of five), computing the standard deviation for the seven replicate concentrations. and multiplying this value by 3.14 (the Student's t value for 99 percent confidence for seven values).

1.0 DATA COMPLETENESS FOR VOA ANALYSIS IN AIR

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of volatile data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Documentation Completion (Form Is and Laboratory Case File, Narrative or Notices)

1.3.1 Were the correct units indicated, mg/m^3 for air?

1.3.2 Were raw data to support analyses and QC operations present and complete?

ACTIONS: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.4 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then flag all positive results with a "J" and all non-detects "UJ".

1.6 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.7 Were field cartridge blanks, equipment blanks, volume pairs, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

Samples should be refrigerated at <4°C in a clean environment during storage and analyzed within 30 days of sample collection (within one week for limonene, carene, bis-chloromethyl ether and labile sulfur or nitrogen-containing volatiles). Samples taken on tubes containing multiple sorbent beds should be analyzed as soon as possible after sampling unless it is know in advance that storage will not cause significant sample recovery errors.

2.1 Method TO-17: Air samples analyzed within 30 days of sample collection.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

VALIDATION ACTIONS:

a. If holding times are exceeded associated sample results are flagged as estimated (UJ, J).
b. If correct preservation was not used, associated sample results are flagged as estimated (UJ, J).
c. If holding times are grossly exceeded (more than twice the requirements), associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected, R.

2.2 Summarize below samples qualified due to holding time excursions.

Sample ID (Client/lab)	Date Collected	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogate compounds prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the purge and trap gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries.
The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples?

3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

Percent recovery = conc found/conc spiked * 100

VALIDATION ACTIONS: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).

b. If %recovery is 10%-upper control limit, flag associated sample results and detection limits as estimated (UJ,J).

c. If %recovery is > upper control limit, flag **positive** results as estimated (J).

d. If surrogates not used or not evaluated contact laboratory for explanation and describe problems/resolutions in final narrative report.

e. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.3 List below samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action
Note:			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs then evaluated

4.1 Were MS/MSDs analyzed and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Were laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.
RPD = I R1-R2I/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are approximated (J).

b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.

c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).

c. If RPD criteria are not met, approximate **detected** results (J) and non detected results approximate (UJ).

d. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

4.4 List all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limits]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for Laboratory Control Samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. The LCS must be extracted and analyzed concurrently with the samples in the batch, using the same instrumentation as the samples. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include new LCS analysis.

5.1 Were LCSs analyzed? Check the QAPP for frequency of LCS.
5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).

b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).

c. If LCS recoveries <10%, reject detection limits R, approximate detected results (J).

d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client/lab ID)

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks and field blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

Laboratory method blanks are analyzed at least once in every 24 hour analytical sequence and are unused, certified canisters that have not left the laboratory. The laboratory method blank must be analyzed before any samples are analyzed.
Acceptance criteria includes the following:
Area response for each internal standard must be within 40% of the mean area response of the internal standard in the most recent calibration.
The retention time for each internal standard must be within 0.33 minutes between the blank and the most recent calibration.
The blank should not contain any target analytes at a concentration greater than its quantitation level and should not contain additional compounds that would interfere with identification of a target analyte.

Laboratory blanks must be identically packed tubes, from the same batch, with similar history and conditioned at the same time as the tubes used for sample collection. At least two are required per monitoring exercise. They must be stored in the laboratory in clean controlled conditions (<4°C) throughout the monitoring program and analyzed at the same time as the samples-- one at the beginning and one at the end of the sequence of runs.

Field blanks are the same as laboratory blanks except that they are transported to and from the monitoring site, are uncapped and immediately resealed at the monitoring site, but do not actually have air pumped through them. One field blank tube is taken for every ten sampled tubes on a monitoring exercise and no less than two field blanks should be collected, however small the monitoring study. The field blanks should be distributed evenly throughout the set of sampled tubes to be analyzed.

Backup tubes may be required to determine the cause of any problem if performance criteria are not met. Back-up tubes (identical to those used for sample collection) should be used to investigate situations in which distributed volume pairs do not agree within acceptable tolerance. To use back-up tubes, a second identical sampling tube is placed in series with a primary (front) tube. The purpose of the backup tube is to capture compounds that pass through the primary tube because of breakthrough. Analysis of the backup tube may indicate unexpected breakthrough or give evidence of channeling of sample through the tube because of loose packing.

Note: B flags applied by the lab should not be removed from Form 1s.

6.1 Were laboratory blanks analyzed for each group of samples?
6.2 Did the laboratory method blank meet acceptance criteria?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Inform PM immediately.

6.2 Field Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.2.1 Were field blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

6.3 Were tentatively identified compounds reported? Were they detected in any of the blanks analyzed? TIC results are treated in the same manner as the target compounds in blanks.

6.4 Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected. The target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

Actions levels are calculated at 5x blank value and 10x for methylene chloride, acetone, 2-butanone. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

VALIDATION ACTIONS:
Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the data validation report.

If the sample concentration is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".

b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".

c. If the sample concentration is > Action level, qualification of data is not necessary.

6.5 Were back up cartridges <20% of the concentration of compounds present in the first cartridge or equal to the concentration in the blank cartridge?

VALIDATION ACTIONS: Note in the data validation report.

6.6 There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, he/she should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. In this case, the "5x" or "10x" rules may not apply; the target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

6.7 If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as unusable (R) due to interference. This should be noted for action if the contamination is suspected of having an effect on the sample results.

6.8 Instrument blanks should be analyzed after high concentrations; otherwise carryover may be suspected.

6.9 List all blanks and any samples qualified due to blank contamination.

Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank ID	Compound	Concentration.	Action Level	Samples Affected (client/lab ID)

7.0 GC/MS TUNING CRITERIA

Tuning and performance criteria are established to verify GC/MS performance; to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.
Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is performed using a single scan no more than 20 scans prior to the elution of BFB (not part of the BFB peak). Other documented approaches suggested by the instrument manufacturer may be used. The following table provides criteria to follow. Otherwise, other tuning criteria may be used if method performance is not adversely affected. The samples, standards and associated QC samples must be analyzed using the same tune conditions, within the 12 hour clock that is started at the time of injection of the BFB solution.

7.1 Were GC/MS tuning performances for 50-ng injection of BFB analyzed for every twelve hours of sample analysis for each GC/MS instrument used?

7.2 Have the ion abundance criteria documented by the method been met for each tune (verify that ion abundance's have been normalized to m/z 95)?

7.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

7.4 Are the spectra of the mass calibration acceptable?

7.5 Was the tune performance standard injected at the beginning of the analytical sequence and were all the samples analyzed within the 12-hour clock?

VALIDATION ACTIONS:

a. If tuning has not been done, reject (R) associated sample data and contact laboratory for explanation. Discuss in data completeness section in the data validation report.
b. If no for 7.2, 7.4, or 7.5 reject associated sample results.
c. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described above, then additional information on the instrument performance checks should be obtained. If the techniques employed are found to be at variance with the method, the performance and procedures of the laboratory may merit evaluation. If the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than the BFB peak), then this should be noted for action.

The critical ion abundances are m/z 95/96, 174/175, 174/176, 176/177. Less important are relative abundances of 50 and 75.

4-Bromofluorobenzene Ions and Abundance Criteria for 8260B	
Mass	**Ion Abundance Criteria**
50	8-40 percent of the base peak
75	30-66 percent of the base peak
95	base peak, 100 percent relative abundance
96	5-9 percent of the base peak
173	less than 2 percent of mass 174
174	50-120 percent of the base peak
175	4-9 percent of mass 174
176	93-101 percent of mass 174
177	5-9 percent of mass 176

7.5 List all tunes and any samples qualified due to tune excursions

INSTRUMENT ID:

Unique Tune ID (Date/Time)	Comments	Tune Met	Samples Affected (client/lab ID)

8.0 GC/MS INITIAL CALIBRATION

Calibration criteria has been established to verify that GC/MS is capable of producing acceptable quantitative data. Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the target compound list. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.
All target compounds must have corresponding initial and continuing calibrations.

A minimum of five concentrations of standards with concentrations that span the monitoring range of interest. One standard must be at the sample concentration as the daily calibration standard, and one at the detection limit.
Use internal standards bromochloromethane, chlorobenzene-d5, 1,4-dichlorofluorobenzene at 10 ppbv. The internal standard is introduced into the GC trap during the collection step.

RRF = Comp response *IS concentration/IS response * Comp conc

The calculated %RSD for the RRF for each compound must be less than 30% with at most two exceptions up to a limit of 40%.
The retention time should agree within 0.06 relative retention time units in each calibration standard.
The area response at each calibration level must be within 40% of the mean area response over the calibration range for each internal standard.
The retention time shift for each internal standard must be within 20 seconds of the mean retention time over the initial calibration range for each internal standard.

8.1 Were initial calibrations performed at the required concentrations prior to sample analysis, whenever GC/MS system is modified, and whenever continuing calibration criteria are exceeded?

VALIDATION ACTIONS:

a. If initial calibration data can not provided, reject associated sample data (R).
b. If RRT criteria is not met, approximate detected and non-detected results (UJ, J).
c. If %RSD > criteria approximate detected and non-detected results (UJ, J).

8.2 Check for transcription/calculation errors; check a minimum of one compound to verify that calibration factors and %RSDs have been calculated correctly using the internal standard. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Show calculations below.

Primary Ions of USEPA Method TO-17	
Primary Ion	**Analyte**
*	Dichlorodiflouromethane
50	chloromethane
62	vinyl chloride
94	bromomethane
64	chloroethane
*	Trichlorofluoromethane
96	1,1-dichloroethene
841	methylene chloride
*	Trans-1,2-dichloroethene
63	1,1-dichloroethane
*	2,2-dichloropropane
61	Cis-1,2-dichloroehthene
83	chloroform
*	bromochloromethane
97	1,1,1-trichloroethane
*	1,1-dichloropropyplene
117	carbon tetrachloride
62	1,2-dichloroethane
78	benzene
95	trichloroethene
63	1,2-dichloropropane
83	bromodichloromethane
107	dibromomethane
75	trans-1,3-dichloropropene
92	toluene
75	cis-1,3-dichloropropene
83	1,1,2-trichloroethane
75	1,3-dichloropropane
164	tetrachloroethene
129	dibromochloromethane
*	1,2-dibromomethane
112	chlorobenzene
*	1,1,1,2-Tetrachloroethane
91	ethylbenzene
91	m&p-xylene
91	0-xylene
104	styrene
105	isopropylbenzene
173	bromoform
83	1,1,2,2-Tetrachloroethane
*	1,2,3-Trichloropropane
*	n-propylbenzene
*	bromobenzene
*	1,3,5-trimethylbenzene
*	2-chlorotoluene
*	4-chlorotoluene

*	t-butylbenzene
*	1,2,4-trimethylbenzene
*	s-butylbenzene
*	p-isopropyltoluene
*	1,3-dichlorobenzene
146	1,4-dichlorobenzene
*	n-butylbenzene
*	1,2-dichlorobenzene
*	1,2-dibromo-3-chloropropane
*	1,2,4-trichlorobenzene
225	hexachlorobutadiene
*	naphthalene
*	1,2,3-trichlorobenzene
58	acetone
72	2-butanone
43	vinyl acetate
100	4-methyl-2-pentanone (MIBK)
43	2-hexanone
76	carbon disulfide
Note: * indicates primary ion not available in method	

8.2 List below all initial calibrations and samples qualified for initial calibration excursions.

INSTRUMENT ID:

Unique IC ID (Date)	Compound	RF [control limit] %RSD [control limits]	Action	Samples Affected (client/lab ID)

9.0 CONTINUING CALIBRATION/VERIFICATION

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Continuing calibration checks satisfactory performance of the instrument on a day-to-day basis.

The initial calibration is verified once every 24 hours on a GC/MS system that has met tuning criteria. The continuing calibration standard is at the 10 ppbv level and should contain all target analytes. The %D for each target compound must be within 30%. Daily calibration acceptance criteria must be met before any field samples or blanks are analyzed.

9.1 Were continuing calibration standards analyzed for each 24 hours of sample analysis, for each analyte, for each GC/MS?

9.2 Was the continuing calibration standard compared to the correct initial calibration?

VALIDATION ACTIONS:

a. If no, contact laboratory for explanation and review in data completeness section. Reject associated sample data if continuing calibration data can not be provided (R).

b. If %D > criteria approximate detected and non-detected sample results (UJ,J).

9.3 Check for transcription/calculation errors; check a minimum of one compound to verify that calibration factors have been calculated correctly. Request corrections from the laboratory. Show calculation below.

9.4 List below all continuing calibrations and samples qualified due to continuing calibration excursions.

INSTRUMENT ID:

Unique CC ID (Date)	Compound	RRF [control limit] %D [control limit]	Action	Samples Affected (client/lab ID)

10.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity; (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

Area response for each internal standard must be within 40% of the latest daily calibration or the mean area response of the internal standard in the most recent calibration.
The retention time for each internal standard must be within 20 seconds between the sample and the most recent calibration.
The blank should not contain any target analytes at a concentration greater than its quantitation level and should not contain additional compounds that would interfere with identification of a target analyte.

10.1 Were internal standard areas of samples or blanks within area criteria?

VALIDATION ACTIONS:

a. If area count is above the limit, approximate (J) detected results for compounds quantitated with that internal standard.

b. If area count is below limits, approximate detected and nondetected results (UJ,J) for compounds quantitated with that internal standard.

c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R) and approximate detected results (J).

10.2 Are retention times of the internal standards within 20 seconds of the associated calibration standard?

VALIDATION ACTION:

If retention times are outside criteria, reject undetected results, R, for compounds quantitated with that internal standard. Be aware that false positive and negative results may exist so carefully examine chromatographic profile.

10.3 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	Internal Standard	Internal Area and %R	Range (area)	Action

11.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

11.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate ID	Compound	RPD

12.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION, AND SYSTEM PERFORMANCE

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present). The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand represent an absence of data and are, therefore, more difficult to assess. One example of detecting false negatives is the not reporting of a Target Compound that is reported as a TIC.
For quantitation evaluation, the objective is to ensure that the reported quantitation results and the detection limits are accurate.

For 8260, the qualitative identification of analytes is based on retention time, and on comparison of the sample mass spectrum to a reference mass spectrum generated by the lab using the conditions of the method.
1. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

a. The characteristic ions are the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum

b. The relative intensities of the characteristic ions must agree within + 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)

c. Structural isomers that produce similar mass spectra should be identified as individual isomers if they have different retention times. Resolution is achieved if the height of the valley between two peaks is less than 25% of the sum of the two peak heights.

d. Identification is hampered when sample components are not resolved and produce mass spectra containing ions contributed by more than one analyte. Appropriate selection of sample spectra and background spectra is important.

e. Examination of extracted ion current profiles can aid in the selection of spectra. When analytes coelute the identification may be met, but each spectrum will contain extraneous ions contributed by the coeluting compound.

The field sample peaks should be within the calibration range.
The retention time for each internal standard must be within 0.33 minutes of the retention time of the internal standard in the most recent calibration.

12.1 Were the VOA reconstructed ion chromatograms, the mass spectra for the identified compounds, and the data system printouts included?
If no, contact laboratory and summarize problems and resolutions in data completeness section.

12.2 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other________________________________?
ACTIONS: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement to qualify data.

12.3 Were sample concentrations above the calibration range?
ACTION: Sample results quantitated with responses that exceed calibration range are approximated (UJ,J).

12.4 Were correct quantitation ions used?

Sample calculation:
For TO17 Concentration (mg/m^3) = Area analyte * Conc IS /Area IS*RRF from IC* Volume of sample collected (L)

ppmV = mg/m^3 * 24.45/target analyte molecular weight

Approximately 10% of data should be verified through raw data review. Show calculations below.

12.5 Was the complete target compound list reported for each sample result?

13.0 TENTATIVELY IDENTIFIED COMPOUNDS (TICs)

Note: TICs may not be required for the project. If required for the project, non-target analytes of apparent greatest concentration may be tentatively identified via library search.
Chromatographic peaks in volatile analyses, including blanks, that are not target analytes, surrogates, or internal standards are potential tentatively identified compounds (TICs). TICs must be qualitatively identified via a forward search of the Spectral Library, and the identifications assessed by the data reviewer.

For each sample, the laboratory must conduct a mass spectral search of the library and report the possible identity for the appropriate number of the largest volatile fraction peaks which are not surrogates, internal standard, or target compounds, but which have area or height greater than the area or height of the nearest internal standard.

Guidelines for tentative identification are as follows:
a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.
b. The relative intensities of the major ions should agree within "20% between the sample and the reference spectra.
c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target compounds.
f. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Library reductions can sometimes create these discrepancies.

The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.
Examples:
a. Common laboratory contaminants: CO (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 µg/L or 4000 µg/Kg.
b. Solvent preservatives such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexenone, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.
c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

Occasionally, a target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.
TIC results which are not sufficiently above 10x the level in the blank should not be reported.

13.1 Was library searching required for the project?
13.2 Were Tentatively Identified Compounds properly identified with scan number or retention time, estimated concentration?
13.3 Were the mass spectra for TICs and associated "best match" spectra included?
13.4 Were each of the ions present in the reference mass spectra with a relative intensity greater than 10% also present in the sample mass spectrum?
13.5 Did TIC and "best match" standard relative ion intensities agree within 20%?
13.6 Were TICs quantitated using the closest internal standard free of contamination and using a RRF of 1.0?

Use professional judgement to determine acceptability of TIC identifications. If it is determined that an incorrect identification was made, note below qualifications made to the sample data.

ACTIONS:

1. All TIC results should be qualified "NJ", tentatively identified, with approximated concentrations.
2. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.
3. If all peaks were not library searched and quantitated, these data are requested from the laboratory.
4. If errors are large, request resubmittal of data package.

13.7 Summarize TICs qualified as a result of TIC excursions if required.

Sample ID	TIC	Concentration	Action

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form
USEPA Method TO-17 (8260B) Volatile Organics In Air

Date:____________________ **Number of samples and compounds per sample:**______________

Project Number:______________________________________ **Trip Blanks:**______________

Validator:____ **Equipment Blanks:**_________

Project: ____ **Blind/Field Duplicates:**______

Laboratory:____ **MS/MSDs:**_______________

QAPP:__________________________________ **DV Guidelines: USEPA Region V**

Laboratory package number:__________________ **PARTIAL VALIDATION**

Method reference:

- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes,* Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition.* Washington, D.C.

CT	Sample, EB, MS/MSD, FD Identification	Date collected 1999 2000	Date received 1999 2000	Method TO17	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number
MS/MSD indicates matrix spike/matrix spike duplicate

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
For Analyses of Volatile Organics by USEPA Method TO-17 (Air)

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*. Chicago, Illinois
- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*, Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- USEPA. 1994 *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. EPA-540/R-94/012. Washington D.C.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington. D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA Method TO-17. (Region V guidelines apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is Not Reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR VOA ANALYSIS IN AIR

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues with sample receipt or condition of samples.

1.2 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then flag all positive results with a "J" and all non-detects "UJ".

1.3 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.4 Were field cartridge blanks, equipment blanks, volume pairs, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

Samples should be refrigerated at <4°C in a clean environment during storage and analyzed within 30 days of sample collection (within one week for limonene, carene, bis-chloromethyl ether and labile sulfur or nitrogen-containing volatiles). Samples taken on tubes containing multiple sorbent beds should be analyzed as soon as possible after sampling unless it is know in advance that storage will not cause significant sample recovery errors.

2.1 Method TO-17: Air samples analyzed within 30 days of sample collection.

VALIDATION ACTIONS:

a. If holding times are exceeded associated sample results are flagged as estimated (UJ, J).
b. If correct preservation was not used, associated sample results are flagged as estimated (UJ, J).
c. If holding times are grossly exceeded (more than twice the requirements), associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected, R.

2.2 Summarize below samples qualified due to holding time excursions.

Sample ID (Client/lab)	**Date Collected**	**Date Analyzed**	**Action (number of days out and qualifier)**

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogate compounds prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the purge and trap gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries.
The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples?

VALIDATION ACTIONS: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits (R).

b. If %recovery is 10%-upper control limit, flag associated sample results and detection limits as estimated (UJ,J).

c. If %recovery is > upper control limit, flag **positive** results as estimated (J).

d. If surrogates not used or not evaluated contact laboratory for explanation and describe problems/resolutions in final narrative report.

e. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.2 List below samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action
Note:			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs then evaluated

4.1 Were MS/MSDs analyzed and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Were laboratory batch QC performed?

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected (R), and detected results are approximated (J).

b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.

c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).

c. If RPD criteria are not met, approximate **detected** results (J) and non detected results approximate (UJ).

d. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

4.3 List all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limits]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for Laboratory Control Samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. The LCS must be extracted and analyzed concurrently with the samples in the batch, using the same instrumentation as the samples. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include new LCS analysis.

5.1 Were LCSs analyzed? Check the QAPP for frequency of LCS.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).

b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).

c. If LCS recoveries <10%, reject detection limits R, approximate detected results (J).

d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.2 List all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client/lab ID)

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks and field blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

Laboratory method blanks are analyzed at least once in every 24 hour analytical sequence and are unused, certified canisters that have not left the laboratory. The laboratory method blank must be analyzed before any samples are analyzed.
Acceptance criteria includes the following:
Area response for each internal standard must be within 40% of the mean area response of the internal standard in the most recent calibration.
The retention time for each internal standard must be within 0.33 minutes between the blank and the most recent calibration.
The blank should not contain any target analytes at a concentration greater than its quantitation level and should not contain additional compounds that would interfere with identification of a target analyte.

Laboratory blanks must be identically packed tubes, from the same batch, with similar history and conditioned at the same time as the tubes used for sample collection. At least two are required per monitoring exercise. They must be stored in the laboratory in clean controlled conditions (<4°C) throughout the monitoring program and analyzed at the same time as the samples-- one at the beginning and one at the end of the sequence of runs.

Field blanks are the same as laboratory blanks except that they are transported to and from the monitoring site, are uncapped and immediately resealed at the monitoring site, but do not actually have air pumped through them. One field blank tube is taken for every ten sampled tubes on a monitoring exercise and no less than two field blanks should be collected, however small the monitoring study. The field blanks should be distributed evenly throughout the set of sampled tubes to be analyzed.

Backup tubes may be required to determine the cause of any problem if performance criteria are not met. Back-up tubes (identical to those used for sample collection) should be used to investigate situations in which distributed volume pairs do not agree within acceptable tolerance. To use back-up tubes, a second identical sampling tube is placed in series with a primary (front) tube. The purpose of the backup tube is to capture compounds that pass through the primary tube because of breakthrough. Analysis of the backup tube may indicate unexpected breakthrough or give evidence of channeling of sample through the tube because of loose packing.

Note: B flags applied by the lab should not be removed from Form 1s.

6.1 Were laboratory blanks analyzed for each group of samples?
6.2 Did the laboratory method blank meet acceptance criteria?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Inform PM immediately.

6.2 Field Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.3 Were field blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work? Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

Actions levels are calculated at 5x blank value and 10x for methylene chloride, acetone, 2-butanone. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same weights, volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

VALIDATION ACTIONS:
Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the

data validation report.

If the sample concentration is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".

b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".

c. If the sample concentration is > Action level, qualification of data is not necessary.

6.4 List all blanks and any samples qualified due to blank contamination.
Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank ID	Compound	Concentration.	Action Level	Samples Affected (client/lab ID)

7.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity; (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

Area response for each internal standard must be within 40% of the latest daily calibration or the mean area response of the internal standard in the most recent calibration.
The retention time for each internal standard must be within 20 seconds between the sample and the most recent calibration.
The blank should not contain any target analytes at a concentration greater than its quantitation level and should not contain additional compounds that would interfere with identification of a target analyte.

7.1 Were internal standard areas of samples or blanks within area criteria?

VALIDATION ACTIONS:

a. If area count is above the limit, approximate (J) detected results for compounds quantitated with that internal standard.

b. If area count is below limits, approximate detected and nondetected results (UJ,J) for compounds quantitated with that internal standard.

c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R) and approximate detected results (J).

7.2 Are retention times of the internal standards within 20 seconds of the associated calibration standard?

VALIDATION ACTION:

If retention times are outside criteria, reject undetected results, R, for compounds quantitated with that internal standard. Be aware that false positive and negative results may exist so carefully examine chromatographic profile.

7.3 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	**Internal Standard**	**Internal Area and %R**	**Range (area)**	**Action**

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.
8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate ID	Compound	RPD

Meeting: Monday, February 7, 2000 – Room A4 (1pm to 3:30 pm)

Attendance:
Pam Cox (PC)
Jeff Banikowski (JB)
Dave Farber (DF)
Tom LaVoy (TL)
Neil Murphy (NM)
Paul Mazerkowitz (PM)
Aamer Raza (AR)
Tom Storrie (TS)
Tom Komar (TK)

The meeting reviewed EVS maps >25 and >50 for soil volume purposes.
Background = 1 pCi/g
State limit 50 pCi/g based on U 238

Soil removal surgically
18,400 cubic feet to 114,500 cubic feet
Basically to remove the 114,500 we will remove 550,000 cubic feet

Options:
1. Removal All
2. Sort and Remove Select Soils
3. Hand Dig (surgical strike) man vs. machine

What can Envirocare of Utah accept?
- PCE/TCE TAGM = 1.4/0.7
- PCE/TCE TCLP 20X rule = 14/10
- PCE/TCE Region 3 Risk Based Standards =

At TAGM Levels
PCE = 64,000 cubic feet of soil (WORST SCENARIO)
TCE = 15,000 cubic feet of soil
State Mandated Levels
U238 >25 = 114,500 cubic feet of soil
U238 >50 = 18,400 cubic feet of soil

STANDARD OF CARE IN THE FIELD IS IMPORTANT TO MINIMIZE SOIL

A portion of the material will have to go to Barnwell, SC (more $, higher limits)
"Hot-spots" removed separately go to Barnwell
all other soil will go to Envirocare of Utah

QU: How close can we cut it to know what goes where?
(could stage inside and sort)
Tom LaVoy will know the instruments
- Beta Probe
- Gamma Instruments
- Portable Sodium Iodide Spectra in field (Bill Hayes Help)
- Sodium Iodide System NYSDEC has
- CANBERRA Equipment

Strategy

1. Profile first foot (plot of surface)
2. Mark on the surface (meters look beyond 1 foot so we would always have a buffer zone)
3. Use a small excavator or bobcat to remove the 1' of soil profiled
4. put "dirty soil" in one pile
5. put "clean" soil in a separate pile
6. begin process again for next interval

Therefore we would have separate strategies for separate site areas:

- Hot spot removal at Golf Course and Air Techniques
- Surgically remove soils at Gilbert
- Hog and Haul all soils at Magazine Distributors

Magazine Distributors

100 x 50 x 12 = 2,200
sheet on a Sunday
excavate the following Sunday and fill immediately
plate top prior to paving
WILL NEED THE MOST UPFRONT INFORMATION HERE

5 Cisterns (giant drywells) in the removal area

What to do with them?
Need to install some other storm water system
sheeting will help
pump the cistern left in-place
construction: some sort of bottom. gravel?
Elevations of cisterns? – tend to perk laterally not just vertically
What happened to the dirt when these were put in

Need to do a source control measure: take up as much as possible

Action Items:

List Concepts (potential strategies)	PC
Price out the concepts / strategies	DF/PC
Risk Assessment	AR
Disposal Areas	PC/JB
- Barnwell	JB
- Envirocare	PC/JB
disposal levels for PCE/TCE	
prices for mixed waste	
Evaluate Loading Docks and Cisterns	PM
Site Visit (wk. 2/14)	
EVS Maps	PC/JB
Volume calc. for PCE/TCE options	
put maps in OBG format	
Treatment level for PERK	
Investigate other similar sites	
Lee Tungston	JB
misc. treatment	TL

Section 11

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method TO-13 (8270C) Semivolatile Organics in Air – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method TO-13 (8270C) Semivolatile Organics in Air – Partial Validation

SECTION 11

O'Brien & Gere Engineers Data Validation Form
USEPA Method TO-13 (8270C) Semivolatile Organics In Air
Date:_____________________ Number of samples and compounds per sample:_______________
Project Number:____
Validator:____Equipment Blanks:________
Project: ____Blind/Field Duplicates:______
Laboratory:____MS/MSDs:_______________
QAPP:___________________________________ DV Guidelines: USEPA Region V
Laboratory package number:__________________FULL VALIDATION
Method reference:

- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-13. The Determination of Benzo(a)pyrene and Other Polynuclear Aromatic Hydrocarbons In Ambient Air Using Gas chromatographic and High Performance Liquid Chromatographic Analysis,* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition.* Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-13	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-13	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Semivolatile Organics in Air USEPA Method TO-13

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data.* Chicago, Illinois
- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-13, The Determination of Benzo(a)pyrene and Other Polynuclear Aromatic Hydrocarbons In Ambient Air Using Gas chromatographic and High Performance Liquid Chromatographic Analysis,* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition.* Washington, D.C.
- O'Brien & Gere. 1999. Quality Assurance Project Plan, Sauget Area 1 Support Plan, Sauget and Cahokia, Illinois, St. Louis, Missouri.

These documents have been modified to specifically reflect the requirements presented in USEPA Method TO-13. (Region V Guidelines apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

Summary of Method

Filters and sorbent cartridges (containing PUF or XAD-2®) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler. Approximately 300 m of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent. The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.

The filters and sorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS.

The eluent is further concentrated by K-D evaporation, then analyzed by GC/MS.

1.0 DATA COMPLETENESS FOR SEMIVOLATILE ANALYSIS IN AIR

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of semivolatile data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, mg/m^3 or total µg per PUF for air?

1.4 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.5 Was appropriate clean-up used (GPC)?

1.6 Were any of the samples diluted? Were dilutions performed when necessary? Note if samples were combined due to dilutions.

1.7 Were raw data to support analyses and QC operations present and complete?

ACTIONS: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.8 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.9 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method TO-13 Air samples must be extracted within 7 days of collection and analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

VALIDATION ACTIONS:

a. If extraction holding times are exceeded, associated sample results are flagged as estimated (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 Summarize below samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries. The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Any time there are two or more analyses for a particular fraction the reviewer must determine which are the best data to report. Considerations should include but are not limited to:
a. Surrogate recovery (marginal versus gross deviation).
b. Technical holding times.
c. Comparison of the values of the target compounds reported in each fraction.
d. Other QC information, such as performance of internal standards.

Percent recovery = conc found/conc spiked * 100

Semivolatile surrogates are grouped as follows:

- Acid extractable: phenol-d6, 2-fluorophenol, and 2,4,6-tribromophenol.
- Base neutral: nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14.

VALIDATION ACTIONS: Qualification of data is necessary if two or more base-neutral or acid surrogates are out of control limits or if any one surrogate compound has a recovery <10%.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits,(R).
b. If %recovery is 10% to lower control limit, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, flag **positive** results as estimated (J).
d. If one acid or base surrogate has a recovery >10%, but less than the lower limit and another acid or base has a recovery greater than the upper limit, flag positive results as estimated (J) and detection limits as estimated (UJ).
e. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Alert Project Manager immediately.
f. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.
g. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
h. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.3 List below samples qualified due to surrogate excursions.

Sample ID (client/lab)	**Surrogate**	**%Recovery [control limits]**	**Action**

Note:
PD6 - phenol-d6
2FP - 2-fluorophenol
246TP - 2,4,6-tribromophenol.
NB – nitrobenzene-d5
2FBP - 2-fluorobiphenyl
TP - terphenyl-d14

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration at a frequency as listed in the QAPP (typically one in 20)?
4.2 Were laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

For 8270 - The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.
RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and non detected results approximate (UJ).
e. If complete fractions (acid/base) have recovery problems, all the target analytes in that fraction may be qualified if the MS did not contain all target analytes.
f. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
g. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.2 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for Laboratory Control Samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. The LCS must be extracted and analyzed concurrently with the samples in the batch, using the same instrumentation as the samples. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch? Check the QAPP for frequency of LCS.

5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
e. If complete fractions (acid/base) have recovery problems, all the target analytes in that fraction may be qualified if the LCS did not contain all target analytes

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	**Compound**	**%Recovery, bias, [control limits]**	**Action**	**Samples Affected (client, lab IDs)**

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contamination.

One PUF cartridge and filter from each batch of 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.
During each sampling episode at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.
During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.
Blank levels should not exceed 10 ng/sample for PCBs.

Note: B flags applied by the lab should not be removed from Form 1s.

6.1 Were method blanks analyzed for each group of samples?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Alert Project Manager immediately.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

6.3 Were tentatively identified compounds reported? Were they detected in any of the blanks analyzed? TIC results are treated in the same manner as the target compounds in blanks.

6.4 There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, he/she should qualify the data. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. In this case, the "5x" or "10x" rules may not apply; the target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

6.5 If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as unusable (R) due to interference. This should be noted for action if the contamination is suspected of having an effect on the sample results.

6.6 If inordinate numbers of other target compounds are found at low levels in the blank(s), it may be indicative of a problem and should be noted for action.

6.7 Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected. The target compound should be reported as not detected, and an explanation of the data qualification should be provided in the data review narrative.

Actions levels are calculated at 5x blank value (10x for phthalates). Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.
Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected.

VALIDATION ACTIONS:
Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the data validation report.
If the sample concentration (extract) is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".

b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".

c. If the sample concentration is > Action level, qualification of data is not necessary.

6.3 Summarize all blanks and any samples qualified due to blank contamination.
Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 GC/MS TUNING CRITERIA

Tuning and performance criteria are established to verify GC/MS performance. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is performed using a single scan no more than 20 scans prior to the elution of DFTPP (not part of the DFTPP peak). Other documented approaches suggested by the instrument manufacturer may be used. The following table provides criteria to follow. Otherwise, other tuning criteria may be used if method performance is not adversely affected. The samples, standards and associated QC samples must be analyzed using the same tune conditions, within the 12 hour clock that is started at the time of injection of the DFTPP solution. 50 ng/µL of decafluorotriphenylphosphine (DFTPP) is used. The standard should also contain ng/µL of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and PCP should not have peak tailing (<5%).

7.1 Were GC/MS tuning performances for 50-ng injection of DFTPP analyzed for every twelve hours of sample analysis for each GC/MS instrument used?

7.2 Have the ion abundance criteria documented by the method been met for each tune (verify that ion abundance's have been normalized to m/z 198)?

7.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

7.4 Are the spectra of the mass calibration acceptable?

7.5 Was the tune performance standard injected at the beginning of the analytical sequence and were all the samples analyzed within the 12-hour clock?

7.6 Did degradation of DDT and evaluation of benzidine and PCP meet criteria?

VALIDATION ACTIONS:

a. If tuning has not been done, reject (R) associated sample data and contact laboratory for explanation. Discuss in data completeness section in the data validation report.
b. If no for 7.2, 7.4, or 7.5 reject associated sample results.
c. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described above, then additional information on the instrument performance checks should be obtained. If the techniques employed are found to be at variance with the method, the performance and procedures of the laboratory may merit evaluation. If the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than the DFTPP peak), then this should be noted for action.

Some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/199 and 442/443 are critical. These ratios are based on the natural abundances of carbon 12 and carbon 13 and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of the resolution adjustment and are very important. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. For instance, if m/z 275 has 40% relative abundance (criteria: 10.0-30.0%) and other criteria are met, then the deficiency is minor. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance for m/z 365 is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 0.75% minimum abundance criteria, the deficiency is not as serious.

Decafluorotriphenylphosphine Ions and Abundance Criteria for 8270C	
Mass	Ion Abundance Criteria
51	30-60 percent of 198
68	Less than 2 percent of 69
70	Less than 2 percent of 69
127	40 to 60% of 198
197	Less than 1 percent of 198
198	Base Peak, 100 percent relative abundance
199	5 to 9 percent of 198
275	10 to 30 percent of 198
365	Less than 1 percent of 198
441	Present but less than 443
442	Less than 40 percent of 198
443	17 to 23 percent of 442

7.5 List all tunes and any samples qualified due to tune excursions.

INSTRUMENT ID:

Unique Tune ID	Date/Time	Comments	Tune Met	Samples affected (client/lab ID) and action

8.0 GC/MS INITIAL CALIBRATION

Calibration criteria has been established to verify that GC/MS is capable of producing acceptable quantitative data. Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the target compound list. Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.
All target compounds must have corresponding initial and continuing calibrations.

For 8270, internal calibration is used. Prepare a minimum of five concentrations of standards, **with one concentration being at or below the project DQO (establishing the method quantitation limit – which must be as low as the regulatory or action limit)** and the remaining concentrations should correspond to the expected range of sample concentrations and should not be greater than the working range of the detector. Use internal standards 1,4-dichlorobenzine-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12 or other compounds that have similar retention times at 40 ng/μg/L or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.2 relative to the internal standards. Area is used to calculate response factors. The internal standard used for calculation should have a retention time closest to the analyte.
RF = Comp response *IS concentration/IS response * Comp conc
The system performance check compounds (SPCCs), which are evaluated for compound stability and degradation caused by contaminated lines or active sites in the system, must meet mean response factor criteria of 0.05: n-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol.
The calibration check compounds (CCCs) , which are evaluated for integrity of the system; high variability may indicate system leaks or reactive sites on the column, acenaphthene, 1,4-dichlorobenzene, hexachlorobutadiene, n-nitroso-diphenylamine, di-n-octyl phthalate, fluoranthene, benzo(a)pyrene, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2-nitrophenol, phenol, pentachlorophenol, 2,4,6-trichlorophenol, must be equal to or less than 30%.
The retention time should agree within 0.06 relative retention time units in each calibration standard.

Linearity – Both linear and nonlinear calibration is allowed. Nonlinear calibration may be necessary for low detection limits.

Linear calibration using average calibration or RF – calibration factors and RFs are a measure of the slope of the calibration relationship and assumes the curve passes through the origin. The factor should not vary with the concentration of the standard. However, when the variation, measured as the relative standard deviation (RSD) is less than or equal to 15%, the use of the linear model is appropriate and the average calibration or RF is used for concentration.
If the RSD of target analytes is greater than 15%, the initial calibration may be acceptable is the mean of the RSDs for all analytes is less than or equal to 15%. This approach will lead to greater uncertainty for those analytes for which the RSD is greater than 15%.

Linear calibration using least squares regression – If the RSD is greater than 15%, or if the analyst so chooses, linearity through the origin cannot be assumed and a linear regression of response verses concentration equation that does not pass through the origin may be used. The instrument response is dependent variable (y) and the concentration is the independent variable (x). The regression will produce the slope and intercept for a linear equation (y=mx+b) where y is the peak area, m is the slope, x is the concentration and b is the intercept. The origin is not forced through zero and do not use the origin as the sixth calibration point. The regression calculation will result in the correlation coefficient – r –, which is a measure of the "goodness of fit". A value of 1.00 is perfect, and for quantitative purposes, r must be greater than or equal to 0.99.

Non-linear calibration – if other approaches don't meet criteria, no more than third order non-linear may be used. First order (linear) requires five standards, second order (quadratic) model requires six standards and third order requires seven standards. The "goodness of fit" of the polynomial equation is evaluated by the weighted coefficient of the determination (COD), which must be greater than 0.99.

8.1 Were initial calibrations performed at the required concentrations prior to sample analysis, whenever GC/MS system is modified, and whenever continuing calibration criteria are exceeded?
Verify that secondary ion quantitation has only been performed when there were sample interferences with the primary ion. If secondary ion quantitation has been performed the laboratory must document reasons in case narrative.

VALIDATION ACTIONS:
Check QAPP criteria for remaining compounds.

a. If initial calibration data can not provided, reject associated sample data (R).

b. If RRF <criteria (SPCC, QAPP for remaining compounds) reject sample detection limits -R - and approximate detected results (J) for the affected compounds.

c. If RSD > criteria (CCC, QAPP for remaining compounds) approximate detected and non-detected results (UJ, J).

8.2 Check for transcription/calculation errors; check a minimum of one compound/internal standard to verify that calibration factors and %RSDs have been calculated correctly using the internal standard. Request correction from the laboratory. Show calculation below.

Initial and continuing calibration criteria for USEPA Method 8270C aqueous and soil				
***Internal standard Primary ion SPCC (S) CCC (C)**	**Analyte**	**Minimum RRF**	**Maximum %RSD**	**Maximum % Difference**
1, 93	Bis(2-chloroethyl) ether	0.05	50	50
1, 45	Bis(2-chloroisopropyl) ether	0.05	50	50
1, 128	2-chlorophenol	0.05	50	50
1, 146	1,3-dichlorobenzene	0.05	50	50
1,146 ,C	1,4-dichlorobenzene	0.05	30	20
1, 146	1,2-dichlorobenzene	0.05	50	50
1, 112	2-flurorphenol (surrogate)	0.05	50	50
1, 117	Hexachloroethane	0.05	50	50
1, 107	2-methylphenol	0.05	50	50
1, 107	4-methylpenol	0.05	50	50
1,70 ,S	n-nitroso-di-n-propylamine	0.05	50	50
1,94 ,C	Phenol	0.05	30	20
1, 99	Phenol-d6	0.05	50	50
2, 93	Bis(2-chloroethoxy) methane	0.05	50	50
2, 127	4-chloroaniline	0.05	50	50
2,107 ,C	4-chloro-3-methylphenol	0.05	30	20
2,162 ,C	2,4-dichlorophenol	0.05	30	20
2, 225,C	Hexachlorobutadiene	0.05	30	20
2, 82	Isophorone	0.05	50	50
2, 142	2-methylnaphthalene	0.05	50	50
2, 128	Naphthalene	0.05	50	50
2, 77	Nitrobenzene	0.05	50	50
2, 82	Nitrobenzene-d8 (surrogate)	0.05	50	50
2,139 ,C	2-nitrophenol	0.05	30	20
2, 180	1,2,4-trichlorobenzene	0.05	50	50
3,154 ,C	Acenaphthene	0.05	30	20
3, 152	Acenaphthylene	0.05	50	50
3, 162	2-chloronaphthalene	0.05	50	50
3, 204	4-chlorophenyl phenyl ether	0.05	50	50
3, 168	Dibenzofuran	0.05	50	50
3, 149	Diethyl phthalate	0.05	50	50
3, 163	Dimethyl phthalate	0.05	50	50
3,184 ,S	2,4-dinitrophenol	0.05	50	50
3, 165	2,4-dinitrotoluene	0.05	50	50
3, 162	2,6-dinitrotoluene	0.05	50	50

3, 166	Fluorene	0.05	50	50
3, 172	2-flurorbiphenyl (surrogate)	0.05	50	50
3,237 ,S	Hexachlorocyclpentadiene	0.05	50	50
3, 65	2-nitroaniline	0.05	50	50
3, 138	3-nitroaniline	0.05	50	50
3, 138	4-nitroaniline	0.05	50	50
3,139 ,S	4-nitrophenol	0.05	50	50
3, 330	2,4,6-tribromophenol (surrogate)	0.05	50	50
3, 196,C	2,4,6-trichlorophenol	0.05	30	20
3, 196	2,4,5-trichlorophenol	0.05	50	50
4, 178	Anthracene	0.05	50	50
4, 248	4-bromophenyl phenyl ether	0.05	50	50
4, 149	di-n-butyl phthalate	0.05	50	50
4, 198	4,6-dinitro-2-methyl-phenol	0.05	50	50
4,202 ,C	Fluoranthene	0.05	30	20
4, 284	Hexachlorobenzene	0.05	50	50
4, 169,C	N-nitrosodiphenylamine	0.05	30	20
4, 266,C	Pentachlorophenol	0.05	30	20
4, 178	Phenanthrene	0.05	50	50
5, 228	Benzo(a)anthracene	0.05	50	50
5, 149	Bis(2-ethylhexyl) phthalate	0.05	50	50
5, 149	Butyl benzyl phthalate	0.05	50	50
5, 228	Chrysene	0.05	50	50
5, 252	3,3'-dichlorobenzidine	0.05	50	50
5, 202	Pyrene	0.05	50	50
5, 244	Terphenyl-d14 (surrogate)	0.05	50	50
5, 149	di-n-octyl phthalate	0.05	50	50
5, 276	Indeno(1,2,3-cd)pyrene	0.05	50	50
6, 252	Benzo(b)fluoroanthene	0.05	50	50
6, 252	Benzo(k)fluroanthene	0.05	50	50
6, 276	Benzo(g,h,I)perylene	0.05	50	50
6, 252,C	Benzo(a)pyrene	0.05	30	20
6, 278	Dibenz(a,h)anthracene	0.05	50	50
	Carbazol	0.05	50	50

Note:
Internal standards are suggested; internal standards used must have retention times that are closest to the analytes:
1 – 1,4-dichlorobenzene-d4
2 – naphthalene-d8
3 – acenaphthene-d10
4– phenanthrene-d10
5 – chrysene-d12
6- perylene-d12

8.3 List all calibrations and samples qualified due to initial calibration excursions.

INSTRUMENT ID:

Unique IC ID	Date	Compound	RRF [control limit] %RSD [control limit]	Action	Samples Affected (client/lab ID)

9.0 CONTINUING CALIBRATION

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Continuing calibration checks satisfactory performance of the instrument on a day-to-day basis. The initial calibration is verified once every 12 hours.

For 8270, a calibration standard near the midpoint concentration of the calibration range must meet the verification criteria. The system performance check compounds (SPCCs), which are evaluated for compound stability and degradation caused by contaminated lines or active sites in the system, must meet mean response factor criteria of 0.05: n-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol.
The calibration check compounds (CCCs), which are evaluated for integrity of the system; high variability may indicate system leaks or reactive sites on the column, acenaphthene, 1,4-dichlorobenzene, hexachlorobutadiene, n-nitroso-diphenylamine, di-n-octyl phthalate, fluoranthene, benzo(a)pyrene, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2-nitrophenol, phenol, pentachlorophenol, 2,4,6-trichlorophenol, must be equal to or less than 20% D, where %D is percent difference when performing the average response factor calibration and percent drift when using a regression calibration. Corrective action must be taken if these criteria are not met prior to the analysis of samples. If the CCCs are not included in the list of analytes for a project, and not included in the standards, all analytes must meet the 20% D criterion.

The retention time of the internal standards must not change by more than 30 seconds from that in the mid-point standard of the most recent initial calibration sequence. Otherwise, corrections must be made and the samples analyzed under this calibration must be reanalyzed. The area of the internal standards must not change by a factor of two (-50% to +100%) from that in the mid-point standard of the most recent initial calibration sequence. Otherwise corrections must be made and the samples analyzed under this calibration must be reanalyzed.

9.1 Were continuing calibration standards analyzed for each twelve hours of sample analysis, for each analyte, for each GC/MS?

VALIDATION ACTIONS:
Check QAPP criteria for remaining compounds.

a. If no, contact laboratory for explanation and review in data completeness section. Reject associated sample data if continuing calibration data can not be provided (R).
b. If RRF <criteria (SPCC, QAPP for remaining compounds) reject sample detection limits (R) and approximate (J) detected results for the affected compounds.
c. If %D > criteria (CCC, QAPP for remaining compounds) approximate detected and non-detected sample results (UJ,J).

9.2 Check for transcription/calculation errors; check a minimum of one compound/internal standard to verify that calibration factors and %Ds have been calculated correctly using the specified internal standard. Request corrections from laboratory. Show calculation below.

9.3 List below all continuing calibrations and samples qualified due to continuing calibration excursions.

INSTRUMENT ID:

Unique CC ID	Date	Compound	RRF [control limit] %D [control limit]	Action	Samples Affected (client and lab ID)

10.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity; (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

For 8270, Internal standards **may** be monitored in all samples, blanks, and standards. The QAPP should be consulted to determine if internal standard evaluation is required for the project. Use internal standards 1,4-dichlorobenzene-d4, napthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 or other compounds that have similar retention times at 40 ng/μL or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.2 relative to the internal standards. Area is used to calculate response factors. Use the internal standard used for calculation should have a retention time closest to the analyte.

10.1 Were internal standard areas of samples or blanks within +100% or -50% of the internal standard associated with the continuing calibration standard?

10.2 Check that correct internal standard data from the calibration standard is used for comparison. If errors are present, a more in-depth review of the data is required. Summarize necessary corrections.

Note: The laboratory is required to reanalyze field, QC, and blank samples when internal standard criteria are not met.

VALIDATION ACTIONS:

a. If area count is above the limit, approximate (J) detected results for compounds quantitated with that internal standard.

b. If area count is below limits, approximate detected and nondetected results (UJ,J) for compounds quantitated with that internal standard.

c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R), approximate detected results (J).

10.2 Are retention times of the internal standards within 30 seconds of the associated calibration standard?

VALIDATION ACTION:
If retention times are outside criteria, reject undetected results, R, for compounds quantitated with that internal standard. Be aware that false positive and negative results may exist so carefully examine chromatographic profile.

10.3 Were samples and method blanks reanalyzed when internal standard criteria was exceeded?

VALIDATION ACTION: Document in the narrative report that the laboratory was not in compliance with analytical method requirements.
If yes, and internal standard areas remain outside criteria, validate both sets of sample data with respect to above actions.

If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:
a. Magnitude and direction of the IS area shift.

b. Magnitude and direction of the IS retention time shift.
c. Technical holding times.
d. Comparison of the values of the target compounds reported in each fraction.
e. Other QC results.

10.4 List samples qualified due to internal standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	**Internal Standard**	**Area and Percent Recovery**	**Range (area)**	**Action**

Note:
Internal standard 1,4-dichlorobenzne-d4 (14DCB)applies to :Bis(2-chloroethyl) ether, Bis(2-chloroisopropyl) ether, 2-chlorophenol, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 2-flurorphenol (surrogate),
Hexachloroethane, 2-methylphenol, 4-methylpenol, n-nitroso-di-n-propylamine, Phenol, Phenol-d6

Internal standard naphthalene-d8 (ND) applies to: 2-Bis(2-chloroethoxy) methane, 4-chloroaniline, 4-chloro-3-methylphenol, 2,4-dichlorophenol, Hexachlorobutadiene, Isophorone, 2-methylnaphthalene, Naphthalene,
Nitrobenzene, Nitrobenzene-d8 (surrogate), 2-nitrophenol, 1,2,4-trichlorobenzene

Internal standard acenaphthene-d10 (AN) applies to: Acenaphthene, Acenaphthylene, 2-chloronaphthalene, 4-chlorophenyl phenyl ether, Dibenzofuran, Diethyl phthalate, Dimethyl phthalate, 2,4-dinitrophenol, 2,4-dinitrotoluene, 2,6-dinitrotoluene, Fluorene, 2-flurorbiphenyl (surrogate), Hexachlorocyclpentadiene, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 2,4,6-tribromophenol (surrogate), 2,4,6-trichlorophenol, 2,4,5-trichlorophenol

Internal standard phenanthrene-d10 (PH) applies to: Anthracene, 4-bromophenyl phenyl ether, di-n-butyl phthalate, 4,6-dinitro-2-methyl-phenol, Fluoranthene, Hexachlorobenzene, N-nitrosodiphenylamine, Pentachlorophenol, Phenanthrene

Internal standard chrysene-d12 (C) applies to: Benzo(a)anthracene, Bis(2-ethylhexyl) phthalate, Butyl benzyl phthalate, Chrysene, 3,3'-dichlorobenzidine, Pyrene, Terphenyl-d14 (surrogate), di-n-octyl phthalate,
Indeno(1,2,3-cd)pyrene

Internal standard perylene-d12 (P) applies to: Benzo(b)fluoroanthene, Benzo(k)fluroanthene, Benzo(g,h,l)perylene, Benzo(a)pyrene, Dibenz(a,h)anthracene

11.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

11.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD

12.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION AND SYSTEM PERFORMANCE

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present). The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand represent an absence of data and are, therefore, more difficult to assess. One example of detecting false negatives is the not reporting of a Target Compound that is reported as a TIC.
For quantitation evaluation, the objective is to ensure that the reported quantitation results and the detection limits are accurate.

Dilutions are performed to keep the analyte concentration in the upper half of the calibration range. The qualitative identification of analytes is based on retention time, and on comparison of the sample mass spectrum to a reference mass spectrum generated by the lab using the conditions of the method.

1. The relative retention times (RRTs) must be within +0.06 RRT units of the standard RRT.
2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

a. The characteristic ions are the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum

b. The relative intensities of the characteristic ions must agree within + 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)

c. Structural isomers that produce similar mass spectra should be identified as individual isomers if they have different retention times. Resolution is achieved if the height of the valley between two peaks is less than 25% of the sum of the two peak heights.

d. Identification is hampered when sample components are not resolved and produce mass spectra containing ions contributed by more than one analyte. Appropriate selection of sample spectra and background spectra is important.

e. Examination of extracted ion current profiles can aid in the selection of spectra. When analytes coelute the identification may be met, but each spectrum will contain extraneous ions contributed by the coeluting compound.

12.1 Were the SVOC reconstructed ion chromatograms, the mass spectra for the identified compounds, and the data system printouts included?
If no, contact laboratory and summarize problems and resolutions in data completeness section.

12.2 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other________________________________?
Actions: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement in quality data.

12.3 Was the RRT of each reported compound within criteria?
RRT= RT analyte/RT internal standard

12.4 Did all the ions present in the mass spectrum meet criteria?
Note: If ions >10% in the sample spectrum are not present in the standard spectrum, verify that these have been accoutered for by the analyst.

12.5 Were sample and standard relative intensities within criteria?
ACTIONS: If no, for any of the above, use professional judgement to determine acceptability of data. If it is determined that incorrect identifications were made, all such data should be rejected (R) or changed to non-detected (U). Summarize qualifications performed below and in the narrative report.

12.6 Were samples reanalyzed at the appropriate dilution, when saturation occurred or when concentrations exceed linear range of the calibration curve?
Note: When sample dilution is performed, the laboratory typically reports two sets of sample data, diluted sample with responses within linear range and undiluted sample (least diluted sample is reported if two sets of dilutions were performed).
ACTION: Sample results quantitated with responses that exceed calibration range are approximated (J). In addition depending on data quality objectives of the project reanalysis of diluted extract may be required. Review resolutions in the narrative report.

12.8 Were correct quantitation ions, internal standard and RF used?

12.9 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions?
ACTIONS: If no and errors are large, request resubmittal of data package.

Sample calculation:

Concentration mg/m^3 =µg/L = Area analyte * Conc IS * Dilution factor * Vol of extract (µl) /Area IS*RF from IC *Volume air sampled (ml)

12.10 Were compounds detected at concentrations below CRQL (or PQL) reported and qualified with a "J"?
Actions: If no, make necessary corrections. Summarize results of raw data review below.

12.11 Was the complete target compound list reported for each sample result?
ACTIONS: If no, request corrections from the laboratory. Summarize necessary corrections.

Document which sample analyses were reviewed and indicate frequency of raw data review. Approximately 10% of data should be verified through raw data review. Show calculations below.

13.0 TENTATIVELY IDENTIFIED COMPOUNDS (TICs)

Note: TICs may not be required for the project. If required for the project, non-target analytes of apparent greatest concentration may be tentatively identified via library search.

Chromatographic peaks in volatile analyses, including blanks, that are not target analytes, surrogates, or internal standards are potential tentatively identified compounds (TICs). TICs must be qualitatively identified via a forward search of the Spectral Library, and the identifications assessed by the data reviewer.

For each sample, the laboratory must conduct a mass spectral search of the library and report the possible identity for the appropriate number of the largest volatile fraction peaks which are not surrogates, internal standard, or target compounds, but which have area or height greater than the area or height of the nearest internal standard.

Guidelines for tentative identification are as follows:
a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.
b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.
c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coelution of additional TIC or target compounds.
e. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Library reductions can sometimes create these discrepancies.

The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.
Examples:
a. Common laboratory contaminants: CO (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2-trifluoroethane or fluoro-trichloromethane), and phthalates at levels less than 100 µg/L or 4000 µg/Kg.
b. Solvent preservatives, such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.
c. Aldol reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

Occasionally, a target compound may be identified as a TIC in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.
TIC results, which are not sufficiently above the level in the blank, should not be reported.

13.1 Was library searching required for the project?
13.2 Were Tentatively Identified Compounds properly identified with scan number or retention time, estimated concentration?
13.3 Were the mass spectra for TICs and associated "best match" spectra included?

13.4 Were each of the ions present in the reference mass spectra with a relative intensity greater than 10% also present in the sample mass spectrum?

13.5 Did TIC and "best match" standard relative ion intensities agree within 20%?

Use professional judgement to determine acceptability of TIC identifications. If it is determined that an incorrect identification was made, note in below qualifications made to the sample data.

13.6 Were TICs quantitated using the closest internal standard free of contamination?
ACTIONS: If no, note corrections below, if errors are large, request resubmittal of data package:

ACTIONS:
1. All TIC results should be qualified "NJ", tentatively identified, with approximated concentrations.
2. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.
3. If all peaks were not library searched and quantitated, these data are requested from the laboratory.
4. If errors are large, request resubmittal of data package.

13.7 Summarize TICs qualified as a result of TIC excursions, if required.

Sample ID	TIC	Concentration

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form
USEPA Method TO-13 (8270C) Semivolatile Organics In Air
Date:______________________ Number of samples and compounds per sample:________________
Project Number:____
Validator:____Equipment Blanks:________
Project: ____Blind/Field Duplicates:______
Laboratory:____MS/MSDs:_______________
QAPP:____ DV Guidelines: USEPA Region V
Laboratory package number:__________________PARTIAL VALIDATION
Method reference:

- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-13. The Determination of Benzo(a)pyrene and Other Polynuclear Aromatic Hydrocarbons In Ambient Air Using Gas chromatographic and High Performance Liquid Chromatographic Analysis,* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition.* Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-13	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-13	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Semivolatile Organics in Air USEPA Method TO-13

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data.* Chicago, Illinois
- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-13, The Determination of Benzo(a)pyrene and Other Polynuclear Aromatic Hydrocarbons In Ambient Air Using Gas chromatographic and High Performance Liquid Chromatographic Analysis,* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition.* Washington, D.C.
- O'Brien & Gere. 1999. Quality Assurance Project Plan, Sauget Area 1 Support Plan, Sauget and Cahokia, Illinois, St. Louis, Missouri.

These documents have been modified to specifically reflect the requirements presented in USEPA Method TO-13. (Region V Guidelines apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation raw data is Not Reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR SEMIVOLATILE ANALYSIS IN AIR

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues regarding problems with sample receipt or condition.

1.2 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.3 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.4 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method TO-13 Air samples must be extracted within 7 days of collection and analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

VALIDATION ACTIONS:

a. If extraction holding times are exceeded, associated sample results are flagged as estimated (UJ, J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than twice the requirements for original or reanalysis, associated sample results are qualified as approximate for positive results (J) and non-detected results are rejected (R).

2.2 Summarize below samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. Laboratory generated control limits are used to evaluate the recoveries. The evaluation of the results of these system monitoring compounds is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgement.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples at the concentrations specified in the analytical method?

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Any time there are two or more analyses for a particular fraction the reviewer must determine which are the best data to report. Considerations should include but are not limited to:
a. Surrogate recovery (marginal versus gross deviation).
b. Technical holding times.
c. Comparison of the values of the target compounds reported in each fraction.
d. Other QC information, such as performance of internal standards.

Semivolatile surrogates are grouped as follows:

- Acid extractable: phenol-d6, 2-fluorophenol, and 2,4,6-tribromophenol.
- Base neutral: nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14.

VALIDATION ACTIONS: Qualification of data is necessary if two or more base-neutral or acid surrogates are out of control limits or if any one surrogate compound has a recovery <10%.

a. If %recovery is <10%, flag positive results as estimated (J) and reject detection limits,(R).
b. If %recovery is 10% to lower control limit, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, flag **positive** results as estimated (J).
d. If one acid or base surrogate has a recovery >10%, but less than the lower limit and another acid or base has a recovery greater than the upper limit, flag positive results as estimated (J) and detection limits as estimated (UJ).
e. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Alert Project Manager immediately.
f. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.
g. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
h. In the special case of a blank analysis with system monitoring compounds out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable system monitoring compound recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for action.

3.2 List below samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action

Note:
PD6 - phenol-d6
2FP - 2-fluorophenol
246TP - 2,4,6-tribromophenol.
NB – nitrobenzene-d5
2FBP - 2-fluorobiphenyl
TP - terphenyl-d14

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed at the required concentration at a frequency as listed in the QAPP (typically one in 20)?
4.2 Were laboratory batch QC performed?

For 8270 - The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. The MS solution can be the same as the LCS and must be different from the calibration standards.
If the MS recovery is outside of criteria and LCS is within criteria, a matrix effect is suspected. If both MS and surrogate recoveries are out of criteria, analytical problems are suspected.

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and non detected results approximate (UJ).
e. If complete fractions (acid/base) have recovery problems, all the target analytes in that fraction may be qualified if the MS did not contain all target analytes.
f. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
g. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.3 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for Laboratory Control Samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. The LCS must be extracted and analyzed concurrently with the samples in the batch, using the same instrumentation as the samples. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

5.1 Were LCSs extracted and analyzed at the required concentration with each analytical batch? Check the QAPP for frequency of LCS.

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Otherwise, the LCS is spiked with the same analytes as the MS and at the same concentration. The LCS solution can be the same as the MS and must be different from the calibration standards.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
e. If complete fractions (acid/base) have recovery problems, all the target analytes in that fraction may be qualified if the LCS did not contain all target analytes

5.2 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks and equipment blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contamination.

One PUF cartridge and filter from each batch of 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.
During each sampling episode at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.
During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.
Blank levels should not exceed 10 ng/sample for PCBs.

Note: B flags applied by the lab should not be removed from Form 1s.

6.1 Were method blanks analyzed for each group of samples?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Alert Project Manager immediately.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

Actions levels are calculated at 5x blank value (10x for phthalates). Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same dilution. It may be easier to work from the raw data sheets for blanks and samples. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.
Instrument blanks should be analyzed after high concentrations- otherwise carryover may be suspected.

VALIDATION ACTIONS:
Field/Equipment blanks are not used to qualify sample data.; analytes detected in these blanks are only noted in the data validation report.
If the sample concentration (extract) is less than 5x/10x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".

b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".

c. If the sample concentration is > Action level, qualification of data is not necessary.

6.4 Summarize all blanks and any samples qualified due to blank contamination.
Note that field/equipment blanks are not used to qualify sample results; analytes detected are only noted in the validation report.

Unique Blank Identification	**Compound**	**Concentration**	**Action Level**	**Samples Affected (client/lab ID) and Action**

7.0 INTERNAL STANDARDS EVALUATION

Internal standard areas are evaluated to assess GC/MS instrument performance and/or loss of sensitivity; (to effectively check drifting method performance, poor injection execution, and the need for system inspection or maintenance), therefore affecting compound quantitation.

For 8270, Internal standards **may** be monitored in all samples, blanks, and standards. The QAPP should be consulted to determine if internal standard evaluation is required for the project. Use internal standards 1,4-dichlorobenzene-d4, napthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 or other compounds that have similar retention times at 40 ng/µL or lower for more sensitive instruments. The internal standard should permit the compounds of interest to have retention times of 0.8-1.2 relative to the internal standards. Area is used to calculate response factors. Use the internal standard used for calculation should have a retention time closest to the analyte.

7.1 Were internal standard areas of samples or blanks within +100% or -50% of the internal standard associated with the continuing calibration standard?

Note: The laboratory is required to reanalyze field, QC, and blank samples when internal standard criteria are not met.

VALIDATION ACTIONS:

a. If area count is above the limit, approximate (J) detected results for compounds quantitated with that internal standard.
b. If area count is below limits, approximate detected and nondetected results (UJ,J) for compounds quantitated with that internal standard.
c. If extremely low area counts are reported (<10%), flag associated detection limits as unusable (R), approximate detected results (J).

7.2 Are retention times of the internal standards within 30 seconds of the associated calibration standard?

VALIDATION ACTION:
If retention times are outside criteria, reject undetected results, R, for compounds quantitated with that internal standard. Be aware that false positive and negative results may exist so carefully examine chromatographic profile.

7.3 Were samples and method blanks reanalyzed when internal standard criteria was exceeded?

VALIDATION ACTION: Document in the narrative report that the laboratory was not in compliance with analytical method requirements.
If yes, and internal standard areas remain outside criteria, validate both sets of sample data with respect to above actions.

If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:
a. Magnitude and direction of the IS area shift.
b. Magnitude and direction of the IS retention time shift.

c. Technical holding times.
d. Comparison of the values of the target compounds reported in each fraction.
e. Other QC results.

7.4 List samples qualified due to internal standard excursions.

INSTRUMENT:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Range (area)	Action

Note:
Internal standard 1,4-dichlorobenzne-d4 (14DCB)applies to :Bis(2-chloroethyl) ether, Bis(2-chloroisopropyl) ether, 2-chlorophenol, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 2-flurorphenol (surrogate),
Hexachloroethane, 2-methylphenol, 4-methylpenol, n-nitroso-di-n-propylamine, Phenol, Phenol-d6

Internal standard naphthalene-d8 (ND) applies to: 2-Bis(2-chloroethoxy) methane, 4-chloroaniline, 4-chloro-3-methylphenol, 2,4-dichlorophenol, Hexachlorobutadiene, Isophorone, 2-methylnaphthalene, Naphthalene,
Nitrobenzene, Nitrobenzene-d8 (surrogate), 2-nitrophenol, 1,2,4-trichlorobenzene

Internal standard acenaphthene-d10 (AN) applies to: Acenaphthene, Acenaphthylene, 2-chloronaphthalene, 4-chlorophenyl phenyl ether, Dibenzofuran, Diethyl phthalate, Dimethyl phthalate, 2,4-dinitrophenol, 2,4-dinitrotoluene, 2,6-dinitrotoluene, Fluorene, 2-flurorbiphenyl (surrogate), Hexachlorocyclpentadiene, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 2,4,6-tribromophenol (surrogate), 2,4,6-trichlorophenol, 2,4,5-trichlorophenol

Internal standard phenanthrene-d10 (PH) applies to: Anthracene, 4-bromophenyl phenyl ether, di-n-butyl phthalate, 4,6-dinitro-2-methyl-phenol, Fluoranthene, Hexachlorobenzene, N-nitrosodiphenylamine, Pentachlorophenol, Phenanthrene

Internal standard chrysene-d12 (C) applies to: Benzo(a)anthracene, Bis(2-ethylhexyl) phthalate, Butyl benzyl phthalate, Chrysene, 3,3'-dichlorobenzidine, Pyrene, Terphenyl-d14 (surrogate), di-n-octyl phthalate,
Indeno(1,2,3-cd)pyrene

Internal standard perylene-d12 (P) applies to: Benzo(b)fluoroanthene, Benzo(k)fluroanthene, Benzo(g,h,I)perylene, Benzo(a)pyrene, Dibenz(a,h)anthracene

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD

Section 12

O'Brien & Gere Engineers. Inc. Data Validation Form – USEPA Method TO-4 (8082) Polychlorinated Biphenyls (PCBs) in Air – Full Validation

O'Brien & Gere Engineers. Inc. Data Validation Form – USEPA Method TO-4 (8082) Polychlorinated Biphenyls (PCBs) in Air – Partial Validation

SECTION 12

O'Brien & Gere Engineers Data Validation Form

USEPA Method TO-4 (8082) Polychlorinated Biphenyls (PCBs) In Air

Date:__________________ Number of samples and compounds per sample:____________

Project Number:____

Validator:____Equipment Blanks:________

Project: ____Blind/Field Duplicates:______

Laboratory:_______________________________________MS/MSDs:_______________

QAPP:___________________________________ DV Guidelines: USEPA Region V

Laboratory package number:__________________FULL VALIDATION

Method reference:

- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement. Method TO-4, Method for the Determination of Organochlorine Pesticides and Polychlorinated Biphenyls In Ambient Air.* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*, 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-4	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-4	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses of PCBs by USEPA Method TO-4

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data*. Chicago, Illinois
- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-4, Method for the Determination of Organochlorine Pesticides and Polychlorinated Biphenyls In Ambient Air*, Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition*. Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA Method TO-4. (Region V Guidelines apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

SCOPE AND APPLICATION

Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid, tissue, and aqueous matrices, using open-tubular, capillary columns with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). The target compounds listed below may be determined by either a single- or dual-column analysis system. The method also may be applied to other matrices such as oils and wipe samples, if appropriate sample extraction procedures are employed.

Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards.
Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS (e.g., Method 8270) is also recommended as a confirmation technique when sensitivity permits.

This method includes a dual-column option that describes a hardware configuration in which two GC columns are connected to a single injection port and to two separate detectors.
The option allows one injection to be used for dual-column simultaneous analysis.
The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study.
Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.).

SUMMARY OF METHOD

A measured volume or weight of sample (approximately 1 L for liquids, 2 to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.
Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds. Instead, use Method 8081.
After cleanup, the extract is analyzed by injecting a measured aliquot into a gas chromatograph with either a narrow- or wide-bore fused-silica capillary column and either an electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).
The chromatographic data may be used to determine the seven Aroclors, selected individual PCB congeners, or total PCBs.

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound. The single-column approach may employ either narrow-bore (# 0.32-mm ID) columns or wide-bore (0.53-mm ID) columns. The dual-column approach generally employs a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach generally employs wide-bore (0.53-mm ID) columns, but columns of other diameters may be employed if the analyst can demonstrate and document acceptable performance for the intended application. A third alternative is to employ dual columns mounted in a single GC, but with each column connected to a separate injector and a separate detector.

Calibration standards for Aroclors

A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample.
Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.
Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors also may be used to determine the calibration factor for each Aroclor when a linear calibration model through the origin is chosen.
Prepare a standard for each of the other Aroclors. The concentrations should generally correspond to the mid-point of the linear range of the detector, but lower concentrations may be employed at the discretion of the analyst.

When PCBs are to be determined as Aroclors, an internal standard is typically not used, and decachlorobiphenyl is employed as a surrogate.

When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts, described below. A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial multi-point calibration is performed using the mixture of Aroclors 1016 and 1260.
Standards of the other five Aroclors are necessary for pattern recognition. When employing the traditional model of a linear calibration through the origin, these standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture has
been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards
In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a multi-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern and linear calibration is employed) and not use the 1016/1260 mixture or the pattern recognition standards. When non-linear calibration models are employed, more than five standards of each Aroclor of interest will be needed to adequately describe the detector response.

A 2-µL injection of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate
sensitivity for the compounds of interest.
Record the peak area (or height) for each congener or each characteristic Aroclor peak to be used for quantitation.
A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.
Late-eluting Aroclor peaks are generally the most stable in the environment.

When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below.
A calibration factor will be determined for each characteristic peak, using the total mass of the Aroclor injected. These individual calibration factors are used to quantitate sample results by applying the factor for each individual peak to the area of that peak.
For a five-point calibration, five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture, e.g., there will be at least 25 separate calibration factors for the mixture. The single standard for each of the other Aroclors will generate at least three calibration factors, one for each selected peak.
If a non-linear calibration model is employed, then additional standards containing each Aroclor of interest will be employed, with a corresponding increase in the total number of calibration factors.

The response factors or calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration, if a linear calibration model is used. This involves the calculation of the mean response or calibration factor, the standard deviation, and the relative standard deviation (RSD) for each congener or Aroclor peak. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the linear calibration models must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors , use the calibration factors from those standards to evaluate linearity.

Retention time windows
Absolute retention times are generally used for compound identification. When absolute retention times are used, retention time windows are crucial to the identification of target compounds, and should be established by one of the approaches described in Method 8000. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows. Other approaches to compound identification may be employed, provided that the analyst can demonstrate and document that they are appropriate for the intended application. When conducting either Aroclor or congener analysis, it is important to determine that common single-component pesticides such as DDT, DDD, and DDE do not elute at the same retention times as the target congeners. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples. Therefore, in conjunction with determining the retention time windows of the congeners, the analyst should analyze a standard containing the DDT analogs. This standard need only be analyzed when the retention time windows are determined. It is not considered

part of the routine initial calibration or calibration verification steps in the method, nor are there any performance criteria associated with the analysis of this standard. If Aroclor analysis is performed and any of the DDT analogs elute at the same retention time as an Aroclor peak that was chosen for use in quantitation (see Sec. 7.4.6), then the analyst must either adjust the GC conditions to achieve better resolution, or choose another peak that is characteristic of that Aroclor and does not correspond to a peak from a DDT analog. If PCB congener analysis is performed and any of the DDT analogs elute at the same retention time as a PCB congener of interest, then the analyst must adjust the GC conditions to achieve better resolution.

Gas chromatographic analysis of sample extracts

The same GC operating conditions used for the initial calibration must be employed for the analysis of samples.

Verify calibration at least once each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring reinjection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not *require* analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

The calibration factor for each analyte calculated from the calibration verification standard (CFv) must not exceed a difference of more than ± 15 percent when compared to the mean calibration factor from the initial calibration curve.

When internal standard calibration is used for PCB congeners, the response factor calculated from the calibration verification standard (RFv) must not exceed a ± 15 percent difference when compared to the mean response factor from the initial calibration. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.).

If this criterion is exceeded for any calibration factor or response factor, use the approach described in Sec. 7 of Method 8000 to calculate the average percent difference across all analytes. If the average of the responses for all analytes is within ±15%, then the calibration has been verified. However, the conditions in Sec. 7 of Method 8000 also apply, e.g., the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the ±15% limit.

If the calibration does not meet the ±15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared.

Inject a measured aliquot of the concentrated sample extract. A 2-µL aliquot is suggested, however the same injection volume must be used for both the calibration standards and the sample extracts. Record the volume injected and the resulting peak size in area units.

Qualitative identifications of target analytes are made by examination of the sample chromatograms.

Quantitative results are determined for each identified analyte (Aroclors or congeners).

If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.

Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

Each sample analysis employing external standard calibration must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour analytical shift), or calibration standards interspersed within the samples. The results from these bracketing standards must meet the calibration verification criteria. Multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that met the QC criteria must be evaluated to prevent misquantitations and possible false negative results, and reinjection of the sample extracts may be required. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis. However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, since the verification standard has demonstrated that the analyte would have been detected if it were present. In contrast, if an analyte above the QC limits was detected in a sample extract, then reinjection is necessary to ensure accurate quantitation. If an analyte was not detected in the sample and the standard response is more than 15% below the initial calibration response, then reinjection is necessary. The purpose of this reinjection is to ensure that the analyte could be detected, if present, despite

the change in the detector response, e.g., to protect against a false negative result.
Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.
Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.
If compound identification or quantitation is precluded due to interferences (e.g., broad, rounded peaks or ill-defined baselines are present), corrective action is warranted. Cleanup of the extract or replacement of the capillary column or detector may be necessary. The analyst may begin by rerunning the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix.

Qualitative identification
The identification of PCBs as either Aroclors or congeners using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Confirmation is necessary when the sample composition is not well characterized. When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed.
When simultaneous analyses are performed from a single injection (the dual-column GC configuration described in Sec. 7.3), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

The results of a single column/single injection analysis may be confirmed, if necessary, on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. That standard may be either the individual congeners, individual Aroclor or the Aroclor 1016/1260
mixture.

When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:
• The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.
• The absence of major peaks representing any other Aroclor.
• The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.).

Quantitation of PCBs as Aroclors
The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample
chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample. Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.
Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. Non-linear calibration may result in different models for each selected peak. A concentration is determined using each of the characteristic peaks, using the
individual calibration factor calculated for that peak, and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor concentrations, then it may be more appropriate to perform the analyses using the PCB congener approach described in this method. If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner,
the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

GC/MS confirmation may be used in conjunction with either single-or dual-column analysis if the concentration is sufficient for detection by GC/MS.
Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than full-scan ion trap or selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10 ng/µL in the final extract, while ion trap or SIM may only require a concentration of 1 ng/µL.

Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

1.0 DATA COMPLETENESS FOR PCB ANALYSIS IN AIR

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of PCB data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, mg/m^3 or total µg per PUF for air?

1.4 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.5 Was appropriate clean-up used? – sulfuric acid/potassium permangate (method 3665)?

1.7 Was single-column and second analysis by GC or GC/MS used or dual-column analysis used?

1.8 Were raw data to support analyses and QC operations present and complete?

Actions: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.9 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.10 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method TO-4: Air samples must be extracted within 7 days of collection and analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

Verify the collection dates, analysis dates using raw data and verify the preservation using the chain of custody and case narrative or sample records.

VALIDATION ACTIONS:

a. If extraction holding times are exceeded associated sample results are flagged as estimated (UJ,J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than 2 times the criteria, nondetected sample results are rejected, (R), and detected sample results are approximated (J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of target and/or non-target analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment. Laboratory generated control limits are used to evaluate the recoveries. Decachlorobiphenyl is used as the surrogate.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples?
3.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

Percent recovery = conc found/conc spiked * 100

3.3 Were the retention times of surrogate in standards, blanks and samples within the calculated retention time windows?
3.4 Was interference present in the surrogate peak?

VALIDATION ACTIONS: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, and no interference is present, flag positive results as estimated (J) and reject detection limits,(R).
b. If %recovery is 10% to lower control limit, and no interference is present, flag associated sample results and detection limits as estimated (UJ,J).
c. If %recovery is > upper control limit, and no interference is present, flag positive results as estimated (J).
d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.
e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.
f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data
g. If surrogate retention times in standards, samples, and blanks are outside of the retention time window, flag associated sample results and detection limits as estimated (UJ,J).

h. If interference was present, qualification of samples due to surrogate excursions is not performed.

i. If zero pesticide surrogate recovery is reported, the reviewer should examine the sample chromatogram to determine if the surrogate may be present, but slightly outside its retention time window. If this is the case, in addition to assessing surrogate recovery for quantitative bias, the overriding consideration is to investigate the qualitative validity of the analysis. If the surrogate is not present, qualify all nondetected target compounds as unusable (R).

j. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.5 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	Surrogate	%Recovery [control limits]	Action
Note: DCBP – decachlorobiphenyl			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed for each group of samples and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?
4.3 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.
RPD = l R1-R2l/(R1+R2/2)*100

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and non detected results are approximate (UJ)..
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.4 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

5.1 Were LCSs extracted and analyzed with each analytical batch? Check the QAPP for frequency of LCS.
5.2 Check for transcription/calculation errors between raw data and the reporting form. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.3 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed to ensure that the GC system and solvents used are free of contamination.

One PUF cartridge and filter from each batch of 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.
During each sampling episode at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.
During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.
Blank levels should not exceed 10 ng/sample for PCBs.

Note for Region V, no “B” flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples?

VVALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.
6.2.1 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

There may be instances when little or no contamination was present in the associated blanks, but qualification of the sample was deemed necessary. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but absent in the undiluted sample result. Since both results are not routinely reported, it may be impossible to verify this source of contamination. However, if the reviewer determines that the contamination is from a source other than the sample, the data should be qualified. In this case, the "5x" rule does not apply; the sample value should be reported as a non-detected target compound, "U". An explanation of the rationale for this determination should be provided in the validation report.

If gross contamination exists (e.g., saturated peaks, "hump-o-grams", "junk" peaks), all affected compounds in the associated samples should be qualified as unusable (R), due to interference. This should be noted in the data validation report, and as an action item if the contamination is suspected of having an effect on the sample results.

If inordinate amounts of target herbicides or other interfering non-target compounds are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted for action.

If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgement should be used to determine if instrument cross-contamination has affected any positive compound identification(s), and if so, detected compound results should be qualified.

Actions levels are calculated at 5x blank value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.

VALIDATION ACTIONS:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.3 List all blanks and samples qualified due to blank contamination.
Note for Region V: Equipment/Field blanks are not used for qualification of samples; list the contaminants only.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

7.0 GC INITIAL CALIBRATION AND CALIBRATION VERIFICATION

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide compounds. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence and of producing a linear calibration curve.

Calibration verification checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To confirm the calibration and evaluate instrument performance, calibration verification is performed.

Calibration standards should be prepared at a minimum of five concentrations which correspond to the expected range of concentrations in the samples and should bracket the linear range of the detector. One of the concentrations should be at a concentration near, but above, the method detection limit.

Calibration verification is performed every shift for all target analytes.

Retention time windows are established for compound identification. Three injections of analyte single and multi-component standards over a 72 hour period. The width of the retention time window is ± 3 times the standard deviation of the mean absolute retention time established during the 72 hour period. The absolute retention time for each analyte and surrogate from the calibration verification standard or the mid-point initial calibration standard establishes the center of the retention time window. Each analyte in each standard must fall within its retention time window.
Internal standard may be used for quantitation

Either single-column or dual column analysis may be performed. Compound identification based on single-column should be confirmed on a second column or GC/MS Method 8270 can be used. GC/MS confirmation will require 10 ng/µg in the final extract.

The Percent Relative Standard Deviation (%RSD) of the calibration factors for each of the single component pesticides and surrogates in the initial calibration on both columns must be less than or equal to 20.0 percent. Otherwise, a calibration curve or a non-linear calibration (polynomial equation) must be used.

Calibration verification is performed every shift for all target analytes. The calibration factor should not exceed ± 15% difference.

Identification of PCBs is based on chromatographic pattern. Quantitate PCB residues by comparing total area or height of residue peaks to the total area or height from reference materials. Measure total area or height response from common baseline under all peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. Those peaks must also be present in the chromatogram of the reference materials.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass in nanograms

Concentration (mg/m^3) = µg/L (micrograms of compound per liter of air sampled
= Area analyte * Dilution factor * Vol of extract (µl)
/mean CF (IC) *Vol air sample * Vol extract injected (µl)

Check for transcription/calculation errors for calibration factors, %RSDs, and %Ds. If errors are present, a more in-depth review of the data is required. Request corrections from the laboratory. Summarize necessary corrections.

7.1 VALIDATION ACTIONS:
a - If retention time windows, are not calculated correctly, contact laboratory for corrected resubmission of the data package with corrected windows; use the corrected values for all evaluations.

b - If the sample concentration exceeds the linearity of the calibration curve, and the sample is not properly diluted and re-analyzed, flag the positive results "J".

c - If the standard concentration criteria are not met, flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

d -If the %RSD criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

e - If the %D criteria are not met for the compound(s) being quantified, qualify all associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

f - Do all standard retention times fall within the windows established during the Initial Calibration?
ACTION: If no, associated samples in the entire analytical sequence are potentially affected. Check to see if the sample chromatograms contain peaks within an expanded window surrounding the expected retention times. If no peaks are found and the surrogates are visible, non-detects are valid. If peaks are present and cannot be identified through pattern recognition or using a revised RT window, qualify all positive results "JN" and non-detects as unusable (R). If the retention time windows are grossly exceeded, this should be noted in the data validation report. Retention time windows should be checked for calculation errors and corrections should be requested from the laboratory.

g – Was the correct analytical sequence used for calibration verification analyses?
ACTION: If no flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

7.2 List below all initial calibrations and calibration verifications and list samples qualified due to excursions.

INSTRUMENT ID:

Column ID	Calibration ID - Date/Time	Analyte	Excursion	Samples affected (client/lab ID) and action

8.0 CLEANUP VERIFICATION

Cleanup procedures are utilized to remove matrix interferences from sample extracts prior to analysis. Cleanup procedures *may* be checked by spiking the cleanup columns and cartridges, and verifying the recovery of PCBs through the cleanup procedure.

VALIDATION ACTION:
a - If check criteria are not met, flag associated positive quantitative results with "J" and the sample quantitation limits for non-detected target compounds with "UJ".

8.1 List below samples qualified due to cleanup excursions.

INSTRUMENT ID:

Cleanup ID	Analyte	Excursion	Samples affected (client/lab ID) and action

9.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

9.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?
If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

10.0 TARGET COMPOUND LIST IDENTIFICATION, QUANTITATION AND REPORTED DETECTION LIMITS

VERIFY IDENTIFICATIONS AND QUANTITATION AT APPROXIMATELY A 10% FREQUENCY FOR EACH TYPE OF SAMPLE CALCULATION

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present). The objective is to ensure that the reported quantitative results and contract required quantitation limits (CRQLs) are accurate.

Retention time windows
Absolute retention times are generally used for compound identification. When absolute retention times are used, retention time windows are crucial to the identification of target compounds, and should be established by one of the approaches described in Method 8000. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows. Other approaches to compound identification may be employed, provided that the analyst can demonstrate and document that they are appropriate for the intended application. When conducting either Aroclor or congener analysis, it is important to determine that common single-component pesticides such as DDT, DDD, and DDE do not elute at the same retention times as the target congeners. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples. Therefore, in conjunction with determining the retention time windows of the congeners, the analyst should analyze a standard containing the DDT analogs. This standard need only be analyzed when the retention time windows are determined. It is not considered part of the routine initial calibration or calibration verification steps in the method, nor are there any performance criteria associated with the analysis of this standard. If Aroclor analysis is performed and any of the DDT analogs elute at the same retention time as an Aroclor peak that was chosen for use in quantitation (see Sec. 7.4.6), then the analyst must either adjust the GC conditions to achieve better resolution, or choose another peak that is characteristic of that Aroclor and does not correspond to a peak from a DDT analog. If PCB congener analysis is performed and any of the DDT analogs elute at the same retention time as a PCB congener of interest, then the analyst must adjust the GC conditions to achieve better resolution.

Tentative identification of analytes occurs when a peak in the sample extract falls within the retention time window. Each identification must be confirmed using either a second dissimilar GC column or another technique (GC/MS). The agreement between concentrations should be less than 40% RPD. The higher of the two concentrations should be reported. If one result is significantly higher, check for overlapping peaks and baseline. If no problems are found, report the higher result and note in the case narrative. The retention times of both of the surrogates, matrix spikes, and reported compounds in each sample must be within the calculated retention time windows on both columns.
GC/MS confirmation will require 10 ng/µg in the final extract.

When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract should use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses. Chromatograms should display single component pesticides detected in the sample and the largest peak of any multicomponent analyte detected in the sample at less than full scale.

The calibration factor is:
CF = analyte peak area (or height) in the standard/ analyte mass in nanograms

Concentration (mg/m^3) = µg/L (micrograms of compound per liter of air sampled
= Area analyte * Dilution factor * Vol of extract (µl)
/mean CF (IC) *Vol air sample * Vol extract injected (µl)

VALIDATION ACTION:

Confirm reported detected analytes by comparing the sample chromatograms to the tabulated results and verifying peak measurements and retention times. Confirm reported non-detected analytes by a review of the sample chromatograms. Check the associated blank data for potential interferences (to evaluate sample data for false positives) and check the calibration data for adequate retention time windows (to evaluate sample data for false positives and false negatives).
For multi-component target compounds, the retention times and relative peak height ratios of major component peaks should be compared against the appropriate standard chromatograms.

10.1 If the retention time criteria for both columns were not met, or if interference is present, all target compounds that are reported detected should be considered non-detected.
a. If the misidentified peak was sufficiently outside the target retention time window, then the reported values may be a false positive and should be replaced with the sample CRQL value.
b. If the misidentified peak poses an interference with potential detection of a target peak, then the reported value should be considered and qualified as unusable (R).

10.2 If multi-component target compounds exhibit marginal pattern-matching quality, professional judgement should be used to establish whether the differences are due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of a multi-component pesticide is strongly suggested, results should be reported as presumptively present (N).

10.3 If GC/MS confirmation was required but not performed, the reviewer should report this in the data validation report.

10.4 Quantitation limits affected by large, off-scale peaks should be qualified as unusable (R). If the interference is on-scale, the reviewer can provide an approximated quantitation limit (UJ) for each affected compound.

10.5 Was chromatographic performance acceptable with respect to:
Baseline stability?
Resolution?
Peak shape?
Full scale graph (attenuation)?
Extraneous peaks?
Other_________________________________?
Actions: If no, for any of the above, review below problems and qualification of data that was necessary. Use professional judgement in quality data.

10.6 Were samples reanalyzed at the appropriate dilution, when saturation occurred or when concentrations exceed linear range of the calibration curve?
Note: When sample dilution is performed, the laboratory typically reports two sets of sample data, diluted sample with responses within linear range and undiluted sample (least diluted sample is reported if two sets of dilutions were performed).
ACTION: Sample results quantitated with responses that exceed calibration range are approximated (J). In addition depending on data quality objectives of the project reanalysis of diluted extract may be required. Review resolutions in the narrative report.

10.7 Are the contract required quantitation limits (detection limits) adjusted to reflect sample dilutions?
ACTIONS: If no and errors are large, request resubmittal of data package.

Document which sample analyses were reviewed and indicate frequency of raw data review, approximately 10% of data should be verified through raw data review. Show calculation below:

ADDITIONAL NOTES

O'Brien & Gere Engineers Data Validation Form
USEPA Method TO-4 (8082) Polychlorinated Biphenyls (PCBs) In Air
Date:__________________ Number of samples and compounds per sample:____________
Project Number:____
Validator:____Equipment Blanks:________
Project: ____Blind/Field Duplicates:______
Laboratory:_______________________________________MS/MSDs:_____________
QAPP:___________________________________ DV Guidelines: USEPA Region V
Laboratory package number:_________________PARTIAL VALIDATION
Method reference:

- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-4, Method for the Determination of Organochlorine Pesticides and Polychlorinated Biphenyls In Ambient Air.* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846),* 3rd Edition. Washington, D.C.

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-4	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-4	M	Laboratory ID	PN
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Analyses of PCBs by USEPA Method TO-4

The following worksheets are based on:

- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data.* Chicago, Illinois
- USEPA. 1988 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Air, Second Supplement, Method TO-4, Method for the Determination of Organochlorine Pesticides and Polychlorinated Biphenyls In Ambient Air,* Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development, Research Triangle Park, NC.
- USEPA. 1996. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846), Third Edition.* Washington, D.C.

These documents have been modified to specifically reflect the requirements presented in USEPA Method TO-4. (Region V Guidelines apply to USEPA CLP Methods.)

Table of Contents:

Data Qualifiers

U - The analyte was analyzed for, but was not detected above the reported sample quantitation limit.

J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

N - The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

NJ - The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical represents its approximate concentration.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is Not Reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR PCB ANALYSIS IN AIR

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any issues with sample receipt or condition of samples.

1.2 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.3 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.4 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Method TO-4: Air samples must be extracted within 7 days of collection and analyzed within 40 days of extraction. Samples are stored at 4°C ±2.

VALIDATION ACTIONS:

a. If extraction holding times are exceeded associated sample results are flagged as estimated (UJ,J).
b. If analysis holding times are exceeded, detected sample results are flagged as estimated (J) and nondetected sample results are rejected (R).
c. If extraction holding times are exceeded by more than 2 times the criteria, nondetected sample results are rejected, (R), and detected sample results are approximated (J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 SURROGATE RECOVERY

Surrogates are compounds chemically similar to analytes, but are not expected to occur in samples. Laboratory performance on individual samples is evaluated based on spiking each sample, blank, and QC sample with surrogates prior to sample preparation. Percent recoveries of surrogates are used to evaluate the overall performance of the gas chromatograph system and to evaluate individual sample matrix effects. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences and high concentrations of target and/or non-target analytes. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment. Laboratory generated control limits are used to evaluate the recoveries. Decachlorobiphenyl is used as the surrogate.

3.1 Were surrogates evaluated for each of the samples, blanks and QC samples?

If samples required dilution due to high concentration of target compounds, the surrogates may be diluted such that recoveries can't be measured. If greater than or equal to a five times dilution is used, the sample results are not qualified due to surrogate recovery unless the undiluted analysis of the sample has been qualified due to surrogate recoveries. If the surrogate recoveries are available from a less diluted or undiluted sample result, that may be used to evaluate the surrogate recovery for that sample, but the **reported** sample result must be qualified as described in this section.

VALIDATION ACTIONS: Qualification of data is necessary if one surrogate is out of control limits.

a. If %recovery is <10%, and no interference is present, flag positive results as estimated (J) and reject detection limits,(R).

b. If %recovery is 10% to lower control limit, and no interference is present, flag associated sample results and detection limits as estimated (UJ,J).

c. If %recovery is > upper control limit, and no interference is present, flag positive results as estimated (J).

d. If surrogates are not used contact laboratory for explanation and describe problems/resolutions in final narrative report. Contact Project Manager immediately if surrogates were not evaluated. Use professional judgement in qualifying sample data, if the incorrect concentrations were used.

e. If surrogate recovery is outside of criteria, the lab should perform a reanalysis to confirm that the excursion is due to sample matrix effects rather than the lab deficiency. If the reanalysis was not performed, document in case narrative that the laboratory was not in compliance with SOW requirements.

f. If surrogate recoveries exceeded criteria in the reanalysis, the laboratory is required to report both sets of sample data. Validate both sets of samples results and qualify data

g. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Data is qualified on the professional judgement of the reviewer.

3.2 List below the samples qualified due to surrogate excursions.

Sample ID (client/lab)	**Surrogate**	**%Recovery [control limits]**	**Action**
Note: DCBP – decachlorobiphenyl			

4.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSIS

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

MS/MSD analyses are performed to evaluate effects of sample matrix on method performance. Representative compounds are spiked into field sample prior to sample preparation. Consult the QAPP to determine if the complete target compound list is required for the spiking solution. Percent recoveries and RPDs are then evaluated.

4.1 Were MS/MSDs analyzed for each group of samples and at a frequency as listed in the QAPP (typically one in 20)?
4.2 Was laboratory batch QC performed?

The QAPP may require that the entire target compound list be included in the spiking solution. If the lab did not use the entire list and was required to, note that in the data validation report. Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

VALIDATION ACTIONS: Qualification is limited to the unspiked sample only.

a. If **both** the MS/MSD have <10% recovery for an analyte, detection limits for that analyte are rejected R, and detected results are approximated (J).
b. If **both** MS/MSD recoveries are >upper control limits, detected results are approximated (J). But if % recovery is > upper limit but < 100%, do not qualify results.
c. If **both** MS/MSD recoveries are < lower control limits but >10%, detected and nondetected results are approximated (UJ, J).
d. If RPD criteria are not met, approximate **detected** results (J) and non detected results are approximate (UJ)..
e. If MS/MSDs not analyzed, contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when MS/MSDs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.
f. If it appears that the MS/MSD results indicate a systematic problem, qualify all associated data.

4.3 List below all MS/MSDs and samples qualified due to MS/MSD excursions.

Unique MS/MSD ID	Compound	%Recoveries, bias, [control limits]	RPD [control limit]	Action

5.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSIS

Data for laboratory control samples (LCS) are generated to provide information on the accuracy of the analytical method and the laboratory performance. Laboratory control samples are analyzed to verify that the lab can perform an analysis in a clean matrix. An LCS excursion may indicate extraction or chromatography problems. Corrective actions include the reanalysis of samples or new LCS analysis.

A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself. the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

5.1 Were LCSs extracted and analyzed with each analytical batch? Check the QAPP for frequency of LCS.

VALIDATION ACTIONS: Qualification is performed for specific compounds that exceeded criteria in samples within the same extraction or analytical batch.

a. If LCS recoveries is greater than control limits, approximate detected results (J).
b. If LCS recoveries is less than control limits but >10%, approximate detected and nondetected results (UJ,J).
c. If LCS recoveries <10%, reject detection limits (R), approximate detected results (J).
d. If LCSs not analyzed contact laboratory for explanation and describe problems/ resolutions in final narrative report. Generally, qualification of sample data is not required when LCSs are not at the correct frequency or concentration. Document in the narrative report that the laboratory was not in compliance.

5.2 List below all LCSs and samples qualified due to LCS excursions.

Unique LCS ID	Compound	%Recovery, bias, [control limits]	Action	Samples Affected (client, lab IDs)

6.0 BLANK ANALYSES

Blank analyses are performed and evaluated to assess the existence and magnitude of laboratory and field contamination. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. A method blank is analyzed to ensure that the GC system and solvents used are free of contamination.

One PUF cartridge and filter from each batch of 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.
During each sampling episode at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.
During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.
Blank levels should not exceed 10 ng/sample for PCBs.

Note for Region V, no "B" flag should be removed from the Form 1s.

6.1 Were method blanks analyzed for each group of samples?

VALIDATION ACTIONS: If no, contact laboratory for explanation and review in data completeness section. If blanks are not available, an evaluation of blank contamination can not be made. Reject associated detected results.

6.2 Equipment Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.
6.3 Were equipment blanks collected and analyzed at the frequency specified in the site specific QAPP or Scope of Work?
Note: equipment blanks are usually collected at a minimum frequency of one per 20 field samples.

Actions levels are calculated at 5x blank value. Blank samples **are not** to be qualified with respect to other blanks. Blank evaluation must be done using the same volumes, or dilution. It may be easier to work from the raw data sheets for blanks and samples.

VALIDATION ACTIONS:

If the sample concentration is less than 5x the blank concentration:

a. If the sample concentration is < CRDL (or PQL) and < Action level, report the CRDL (or PQL) with a "U".
b. If the sample concentration is > CRDL (or PQL) and < Action level, report concentration flagged with a "U".
c. If the sample concentration is > Action level, qualification of data is not necessary.

6.4 List all blanks and samples qualified due to blank contamination.
Note for Region V: Equipment/Field blanks are not used for qualification of samples; list the contaminants only.

Unique Blank Identification	**Compound**	**Concentration**	**Action Level**	**Samples Affected (client/lab ID) and Action**

7.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

7.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP? If no, document in the narrative that precision of field sampling methods could not be evaluated.

Summarize below compounds detected in field duplicate samples and the RPDs.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

Section 13

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method TO-9 (8082) Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS in Air – Full Validation

O'Brien & Gere Engineers, Inc. Data Validation Form – USEPA Method TO-9 (8082) Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) SIM/GC/MS in Air – Partial Validation

O'Brien & Gere Engineers Data Validation Form
USEPA Method TO-9 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) In Air (8290)

Date:____________________ Number of samples and compounds per sample:________________
Project Number:____
Validator:____Equipment Blanks:________
Project: ____Blind/Field Duplicates:______
Laboratory:____MS/MSDs:_______________
QAPP:____________________________________ DV Guidelines: USEPA Region II
Laboratory package number:__________________FULL VALIDATION
Method references:

- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Compendium Method TO-9A Determination of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans In Ambient Air.* Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846. 3rd Edition Washington D.C.*

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-9	M	Laboratory ID	P N

Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-9	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms

Method TO-9 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) in Air (8290)

The following worksheets are based on:

- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Compendium Method TO-9A Determination of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans In Ambient Air,* Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- USEPA. 1994 *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS),* Albany, New York.
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd Edition. Washington D.C.*

Table of Contents:

VALIDATION DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the qualifiers assigned to results in the data validation process.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

U - Not detected above the reported detection limit.

NJ - There is presumptive evidence for the presence of the compound at an estimated value.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; cross out sections not applicable to the project.
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

Method TO-9 Information

Scope

This document describes a sampling and analysis method for the quantitative determination of polyhalogenated dibenzo-p-dioxins and dibenzofurans (PHDDs/PHDFs) in ambient air, which include the polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), polybrominated dibenzo-p-dioxins and dibenzofurans (PBDDs/PBDFs), and bromo/chloro dibenzo-p-dioxins and dibenzofurans (BCDDs/BCDFs). The method uses a high volume air sampler equipped with a quartz-fiber filter and polyurethane foam (PUF) adsorbent for sampling 325 to 400 m ambient air in a 24-hour sampling period. Analytical procedures based on high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) are used for analysis of the sample.

Minimum detection limits (MDLs) in the range of 0.01 to 0.2 picograms/meter (pg/m) can be achieved for these compounds in ambient air.

The method does not separately quantify gaseous PHDDs and PHDFs and particulate-associated PHDDs and PHDFs because some of the compounds volatilize from the filter and are collected by the PUF adsorbent. For example, most of the OCDD is collected by the filter and most of the TCDDs are collected by the PUF during sampling. PCDDs/PCDFs may be distributed between the gaseous and particle-adsorbed phases in ambient air. Therefore, the filter and PUF are combined for extraction in this method.

Summary of Method

Quartz-fiber filters and glass adsorbent cartridges are pre-cleaned with appropriate solvents and dried in a clean atmosphere. The PUF adsorbent plugs are subjected to 4-hour Soxhlet extraction using an oversized extractor to prevent distortion of the PUF plug. The PUF plugs are then air dried in a clean atmosphere and installed in the glass cartridges. A 50 microliter aliquot of a 16 picogram/microliter solution of 37Cl4 -2,3,7,8-TCDD is spiked to the PUF in the laboratory prior to field deployment. (Different amounts and additional 13C12 -labeled standards such as 13C12 -1,2,3,6,7,8-HxCDF may also be used if desired.) The cartridges are then wrapped in aluminum foil to protect from light, capped with Teflon® end caps, placed in a cleaned
labeled shipping container, and tightly sealed with Teflon® tap until needed.
For sampling, the quartz-fiber filter and glass cartridge containing the PUF are installed in the high-volume air sampler.
The high-volume sampler is then immediately put into operation, usually for 24 hours, to sample 325 to 400 m3 ambient air.
[Note: Significant losses were not detected when duplicate samplers were operated 7 days and sampled 2660 m3 ambient air.]
The amount of ambient air sampled is recorded at the end of the sampling session. Sample recovery involves placing the filter on top of the PUF. The glass cartridge is then wrapped with the original aluminum foil, capped with Teflon® end caps, placed back into the original shipping container, identified, and shipped to the analytical laboratory for sample processing.
Sample preparation typically is performed on a "set" of 12 samples, which consists of 9 test samples, a field blank, a method blank, and a matrix spike.
The filter and PUF are combined for sample preparation, spiked with 9 13C12 -labeled PCDD/PCDF and 4 PBDD/PBDF internal standards, and Soxhlet extracted for 16 hours. The extract is subjected to an acid/base clean-up procedure followed by clean-up on micro columns of silica gel, alumina, and carbon. The extract is then spiked with 0.5 ng 13C12 -1,2,3,4-TCDD (to determine extraction efficiencies achieved for the C -labeled internal standards) and then concentrated to 10 µL for HRGC-HRMS analysis in a 1 mL conical reactivial.
The set of sample extracts is subjected to HRGC-HRMS selected ion monitoring (SIM) analysis using a 60-m DB-5 or 60-m SP-2331 fused silica capillary column to determine the sampler efficiency, extraction efficiency, and the concentrations or the MDLs achieved for the PHDDs/PHDFs (28).

Defined identification criteria and QA/QC criteria and requirements are used in evaluating the analytical data. The analytical results along with the volume of air sampled are used to calculate the concentrations of the respective tetra- through octa-isomers, the concentrations of the 2,3,7,8-chlorine or -bromine substituted isomers, or the MDLs. The concentrations and/or MDLs are reported in pg/m . The EPA toxicity equivalence factors (TEFs) can be used to calculate the 2,3,7,8- TCDD toxicity equivalents (TEQs) concentrations, if desired.

Sample Recovery

At the end of the desired sampling period, turn the power off. Carefully remove the sampling head containing the filter and adsorbent cartridge to a clean area.
Wrap the combined samples in the original hexane rinsed aluminum foil, attached Teflon® end caps and place them in their original aluminum sample container. Complete a sample label and affix it to the aluminum shipping container.
Chain-of-custody should be maintained for all samples. Store the containers at <4 C and protect from light to prevent possibly photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, refrigerate sample.
Return at least 1 field filter/PUF blank to the laboratory with each group of samples. Treat a field blank exactly as the sample except that

no air is drawn through the filter/adsorbent cartridge assembly.
Ship and store samples under ice (<4 C) until receipt at the analytical laboratory, after which it should be refrigerated at less than or equal to 4 C. Extraction must be performed within seven days of sampling and analysis within 40 days after extraction.

Prepare the sample by extraction followed by cleanup using acid/base, silica column, alumina column, and carbon column techniques.

METHOD 8290 INFORMATION

Scope and Application
Method 8290 method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs) and polychlorinated dibenzofurans tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations.

Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs) considered within the scope of this method that are greater than ten times the upper MCLs must be analyzed by a protocol designed for such concentration levels, e.g. Method 8280.

Summary of Method
This procedure uses matrix specific extraction, analyte specific cleanup and HRGC/HRMS analysis techniques.
If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination.

A specified amount is spiked with a solution containing specified amounts of each of the nine isotopically ($^{13}C_{12}$) labeled PCDDs/PCDFs. The sample is then extracted according to a matrix specific extraction procedure. The extraction procedures are:

The extracts are submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the extracts are cleaned up by column chromatography on alumina, silica gel and activated carbon.

The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding 10 to 50 µL of a nonane solution containing 50 pg/µL of the recovery standards $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners, while the latter is used to determine the percent recoveries of hexa-, hepta-, and octachlorinated PCDD/PCDF congeners.

The µL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

The identification of OCDD and nine of the fifteen 2,3,7,8-substituted congeners for which a 13C-labeled standard is available in the sample fortification and recovery standard solutions, is based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous detection of the two most abundant ions in the molecular ion region.

The remaining six 2,3,7,8-substituted congeners (i.e. 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standards are available in the sample fortification solution, and all other PCDD/PCDF congeners are identified when their relative retention times fall within their respective PCDD/PCDF retention time windows, as established from the routine calibration data, and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD and the simultaneous detection of the two most abundant ions in the molecular ion region. Identification also is based on a comparison of the ratios of the integrated ion abundance of the molecular ion specie to their theoretical abundance ratios.

Interferences
PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes and polychlorinated alkyldibenzofurans, that may be found at concentrations several orders of magnitude higher than the analytes of interest.

A high-resolution capillary column (60 m DB-5, J&W Scientific, or equivalent) is used in this method. However, no single column is known to resolve all isomers. The 60 m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity. In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent.

Reagents and Standard Solutions
High-Resolution Concentration Calibration Solutions – Five nonane solutions containing unlabeled (totaling 17) and carbon-labeled (totaling 11) PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue dependent, with the lowest values for the tetrachlorinated dioxin and furan (1.0 pg/µL) and the highest values for the octachlorinated congeners (1000 pg/µL).
GC Column Performance Check Solution – This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The $^{13}C_{12}$-2,3,7,8-TCDD is also present.
Sample Fortification Solution – This nonane solution contains the nine internal standards at the nominal concentrations. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native

substances. (Note $^{13}C_{12}$-OCDF is not present in the solution.)

Recovery Standard Solution – This nonane solution contains two recovery standards, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, at a nominal concentration of 50 pg/µL per compound. 10 to 50 µL of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

Matrix Spike Fortification Solution – Solution used to prepare the MS and MSD samples. It contains all unlabeled analytes at concentrations corresponding to the HRCC 3.

Procedure

Internal standard addition

Transfer the sample portion to a tared flask and determine its weight.

Add an appropriate quantity of the sample fortification mixture to the sample. All samples should be spiked with 100 µL of the sample fortification mixture to give internal standard concentrations.

Mass Spectrometer

The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less. At a minimum, the ions listed in the method 6 for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection of the molecular ions M and M+2 for ^{13}C-HxCDF and ^{13}C-HpCDF rather than M+2 and M+4 (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in the method. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors.

Data Acquisition

The total cycle time for data acquisition must be ≤ 1 second. The total cycle time includes the sum of all the dwell times and voltage reset times.

Calibration

Initial Calibration – Initial calibration is required before any samples are analyzed for PCDDs and PCDFs. Initial calibration is also required if any routine calibration does not meet the required criteria.

Tune the instrument with PFK.

Inject 2 µL of the GC column performance check solution and acquire SIM mass spectral data.

Analyze a 2 µL portion of each of the five concentration calibration solutions.

The ratio of integrated ion current for the ions must be within the indicated control limits for all unlabeled calibration standards and for carbon-labeled internal and recovery standards.

For each selected ion current profile (SICP) and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 2.5. Measurement of the S/N is required for any GC peak that has an apparent S/N of less than 5:1.

Calculate the 17 relative response factors (RF) for unlabeled target analytes relative to their appropriate internal standards and the nine RFs for the labeled $^{13}C_{12}$ internal standards relative to the two recovery standards according to the following formulae:

$$RF_n = \frac{A_x * Q_{is}}{Q_x * A_{is}} \qquad RF_m = \frac{A_{is} * Q_{rs}}{Q_{is} * A_{rs}}$$

where:

A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDD/PCDFs

A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,

A_{rs} = sum of the integrated ion abundances of the quantitation ions for the labeled recovery standards,

Q_{is} = quantity of the internal standard injected (pg)

Q_{rs} = quantity of the recovery standard injected (pg), and

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected (pg).

The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, and TCDF), the mean RF used will be the same.
NOTE: The calibration solutions do not contain $^{13}C_{12}$-OCDF as an internal standard.
For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer, the mean RF used for those homologous series will be the mean of the RFs calculated for all individual 2,3,7,8-substituted congeners.

Criteria for Acceptable Calibration
The percent relative standard deviations for the mean response factors (RF_n and RF_m) from the 17 unlabeled standards must not exceed ± 20 percent, and those for the nine labeled reference compounds must not exceed ± 30 percent.
The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.
The ion abundance ratios must be within the specified control limits.

Routine Calibration (Continuing Calibration Check) – Routine calibrations must be performed at the beginning of a 12-hour period after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12-hour shift. Inject 2 µL of the concentration calibration solution HRCC-3 standard.

Criteria for Acceptable Routine Calibration – The following criteria must be met before further analysis is performed.
The measured RFs (RF_n for the unlabeled standards obtained during the routine calibration runs must be within ± 20 percent of the mean values established during the initial calibration.
The measured RFs (RF_m for the labeled standards) obtained during the routine calibration runs must be within ± 30 percent of the mean values established during the initial calibration.
The ion abundance ratios must be within allowable control limits.

If either one of the criteria is not satisfied, repeat one more time. If these criteria are still not satisfied, the entire routine calibration process must be reviewed. It is realized that it may not always be possible to achieve all RF criteria. For example, it has occurred that the RF criteria for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD were not met, however, the RF values for the corresponding unlabeled compounds were routinely within the criteria established in the method. In these cases, 24 of the 26 RF parameters have met the QC criteria, and the data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. Corrective action would be in order, for example, if the compounds for which the RF criteria were not met included both the unlabeled and the corresponding internal standard compounds.

Analysis
Inject a 2 µL aliquot of the extract into the GC.
Acquire SIM data
NOTE: The acquisition period must at least encompass the PCDD/PCDF overall retention time window previously determined. Selected ion current profiles (SICP) for the lock-mass ions (one per mass descriptor) must also be recorded and included in the data package. These SICPs must be true representations of the evolution of the lock-mass ions amplitudes during the HRGC/HRMS run.

Identification Criteria
Retention Times

For 2,3,7,8-substituted congeners, which have an isotopically labeled internal or recovery standard present in the sample extract (this represents a total of 10 congeners including OCDD), the retention time (RRT; at maximum peak height) of the sample components (i.e., the two ions used for quantitation purposes must be within –1 to +3 seconds of the isotopically labeled standard.

For 2,3,7,8-substituted compounds that do not have an isotopically labeled internal standard present in the sample extract (this represents a total of six congeners), the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the daily routine calibration results.

For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution.

The ion current responses for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

The ion current responses for both ions used for the labeled standards must reach maximum simultaneously (± 2 seconds).
NOTE: The analyst is required to verify the presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF in the SICPs of the daily performance

checks. Should either one compound be missing, the analyst is required to take corrective action as it may indicate a potential problem with the ability to detect all the PCDD/PCDFs.

Ion Abundance Ratios
The integrated ion currents for the two ions used for quantitation purposes must have a ratio between the lower and upper limits established for the homologous series to which the peak is assigned.

Signal-to-Noise Ratio
All ion current intensities must be ≥ 2.5 times noise level for positive identification of a PCDD/PCDF compound or a group of coeluting isomers.

Polychlorinated Diphenyl Ether Interferences
In addition to the above criteria, the identification of a GC peak as a PCDF can only be made if no signal having a S/N ≥ 2.5 is detected at the same retention time (± 2 seconds) in the corresponding polychlorinated diphenyl ether channel.

Calculations
PCDD or PCDF Compounds

$$C_x = \frac{A_x * Q_{is}}{A_{is} * W * RF_n}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,
A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDD/PCDFs,
A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,
Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,
W = weight, in g, of the sample (solid or organic liquid) or volume in mL of an aqueous sample, and
RF_n = calculated mean relative response factor for the analyte (RFn with n = 1 to 17; Sec 7.7.1.4.5).

Percent recovery of the nine internal standards

$$\text{Internal standard percent recovery} = \frac{A_{is} * Q_{rs}}{Q_{is} * A_{rs} * RF_m} * 100$$

Where:

A_{is} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standard,
A_{rs} = sum of the integrated ion abundances of the quantitation ions for the labeled recovery standard; the selection of the recovery standard depends on the type of congeners
Q_{is} = quantity, in pg, of the recovery standard added to the sample before extraction,
Q_{rs} = quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and
RF_m = calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard. This represents the mean. (RF_m with m = 18 to 26).

If the concentration in the final extract of any of the fifteen 2,3,7,8-substituted PCDD/PCDF compounds exceeds the upper method calibration limits (MCL), the linear range of response versus concentration may have been exceeded.

The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of FC signals included in the homologous total concentration value must be specified in the report.

Sample Specific Estimated Detection Limit – The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-

substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

Samples giving a response for both quantitation ions that is less than 2.5 times the background level.

Use the expression for EDL to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions. of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that peak height.

Use the formula:

$$\text{EDL (specific 2,3,7,8-substituted PCDD/PCDF)} = \frac{2.5 * H_x * Q_{is}}{H_{is} * W\ RF_n}$$

Where:

EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDD/PCDFs.
H_x = sum of the height of the noise level for each quantitation ion for the unlabeled PCDD/PCDFs, measured as shown in Figure 6.
H_{is} = sum of the height of the noise level for each quantitation ion for the labeled internal standard, measured as shown in Figure 6.

Samples characterized by a response above the background level with a S/N of at least 2.5 for both quantitation ions.

When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria, calculate the "**Estimated Maximum Possible Concentration**" (EMPC).

The 2,3,7,8-TCDD **toxicity equivalents** (TE) of PCDDs and PCDFs present in the sample are calculated. This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDD and PCDFs and to OCDD and OCDF. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds.

The concentration of 2,3,7,8-TCDD is calculated from the analysis of the sample extract on the 60 m DB-5 fused silica capillary column.

The concentration of the 2,3,7,8-TCDF is obtained from the analysis of the sample extract on the 30 m DB-225 fused silica capillary column. However, the GC/MS conditions must be altered so that: (1) only the first three descriptors (1.e., tetra-, penta-, and hexachlorinated congeners) are used; and (2) the switching time between descriptor 2 (pentachlorinated congeners) and descriptor 3 (hexachlorinated congeners) takes place following the elution of $^{13}C_{12}$-1,2,3,7,8-PeCDD. The chromatographic separation between the 2,3,7,8-TCDF and its close eluters (2,3,4,7-TCDF and 1,2,3,9-TCDF must be equal or less than 25 percent valley.

For a gas chromatographic peak to be identified as a 2,3,7,8-substituted PCDD/PCDF congener, it must meet the ion abundance and signal-to-noise ratio criteria. In addition, the retention time identification criterion applies here for congeners for which a carbon labeled analogue is available in the sample extract. However, the relative retention time (RRT) of the 2,3,7,8-substituted congeners for which no carbon-labeled analogues are available must fall within 0.006 units of the carbon-labeled standard RRT.

Quality Control

System Performance Criteria – The response factors and mass spectrometer resolving power checks must be performed at the beginning and the end of each 12-hour period during which samples are analyzed. An HRGC/HRMS method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch required more than 12 hours of analyses.

GC Column Performance

The chromatographic separation between 2,3,7,8-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of ≤ 25 percent. The GC column performance check solution also contains the known first and last PCDD/PCDF eluters under the conditions specified in this protocol. The retention times are used to determine the eight homologue retention time windows that are used for qualitative and quantitative purposes. All first eluters of a homologous series should be labeled with the letter F and all last

eluters of a homologous series should be labeled with the letter L.
Switching Times – Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60 m DB-5 column.

Mass Spectrometer Performance
The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12 hour period of operation.

Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. An acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

Performance Check Solutions
At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound.

The continuing calibration and the mass resolution check must be performed also at the end of each 12-hour period. Furthermore, an HRGC/HRMS method blank run must be recorded following a calibration run and the first sample run.

Deviations from criteria specified for the GC performance check or for the mass resolution check invalidate all positive sample data collected between analyses of the performance check solution, and the extracts from those positive samples shall be reanalyzed.

If the continuing calibration check performed at the end of a 12 hour period fails by no more than 25 percent RPD for the 17 unlabeled compounds and 35 percent RPD for the 9 labeled reference compounds, use the mean RFs from the two daily routine calibration runs to compute the analyte concentrations, instead of the RFs obtained from the initial calibration. A new initial calibration (new RFs) is required immediately (within two hours) following the analysis of the samples, whenever the RPD from the end-of-shift routine calibration exceeds 25 percent or 35 percent, respectively.

Duplicate Analyses

The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean).

Matrix Spike and Matrix Spike Duplicate

The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

Percent Recovery of the Internal Standards - For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

Composition of the Sample Fortification and Recovery Standard Solutions[a]

Analyte	Sample Fortification Solution Concentration (pg/μL; Solvent: Nonane)	Recovery Standard Solution Concentration (pg/μL; Solvent: Nonane)
$^{13}C_{12}$-2,3,7,8-TCDD	10	--
$^{13}C_{12}$-2,3,7,8-TCDF	10	--
$^{13}C_{12}$-1,2,3,4-TCDD	--	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	10	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	10	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	--	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	25	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	25	--
$^{13}C_{12}$-OCDD	50	--

(a) These solutions should be made freshly every day because of the possibility of adsorptive losses to glassware. If these solutions are to be kept for more than one day, then the sample fortification solution concentrations should be increased ten fold, and the recovery standard solution concentrations should be doubled. Corresponding adjustments of the spiking volumes must then be made.

The Fifteen 2,3,7,8-Substituted PCDD and PCDF Congeners

PCDD	PCDF
2,3,7,8-TCDD(*)	2,3,7,8-TCDF(*)
1,2,3,7,8-PeCDD(*)	1,2,3,7,8-PeCDF(*)
1,2,3,6,7,8-HxCDD(*)	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD(+)	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDD(*)	1,2,3,4,7,8-HxCDF(*)
	2,3,4,6,7,8-HxCDF
	1,2,3,4,6,7,8-HpCDF(*)
	1,2,3,4,7,8,9-HpCDF

(*) The 13C-labeled analogue is used as an internal standard.
(+) The 13C-labeled analogue is used as a recovery standard.

Isomers of Chlorinated Dioxins and Furans as a Function of the Number of Chlorine Atoms

Number of Chlorine Atoms	Number of Dioxin Isomers	Number of 2,3,7,8 Isomers	Number of Furan Isomers	Number of 2,3,7,8 Isomers
1	2	--	4	--
2	10	--	16	--
3	14	--	28	--
4	22	1	38	1
5	14	1	28	2
6	10	3	16	4
7	2	1	4	2
8	1	1	1	1
Total	75	7	135	10

High-Resolution Concentration Calibration Solutions

Compound	Concentration (pg/µL), Nonane)				
HRCC	5	4	3	2	1
Unlabeled Analytes					
2,3,7,8-TCDD	200	50	10	2.5	1
2,3,7,8-TCDF	200	50	10	2.5	1
1,2,3,7,8-PeCDD	500	125	25	6.25	2.5
1,2,3,7,8-PeCDF	500	125	25	6.25	2.5
2,3,4,7,8-PeCDF	500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDD	500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDD	500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDD	500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDF	500	125	25	6.25	2.5
2,3,4,6,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDD	500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDF	500	125	25	6.25	2.5
1,2,3,4,7,8,9-HpCDF	500	125	25	6.25	2.5
OCDD	1,000	250	50	12.5	5
OCDF	1,000	250	50	12.5	5
Internal Standards	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDD	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	125	125	125	125	125
$^{13}C_{12}$-OCDD	250	250	250	250	250
Field Standards	100	100	100	100	100
$^{37}C_4$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD					
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD[a]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[b]	125	125	125	125	125

(a) Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.
(b) Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF and OCDD internal standards.

PCDD and PCDF Congeners Present in the GC Performance Evaluation Solution Used for Defining the Homologous GC Retention Time Windows on a 60 m DB-5 Column

No. of Chlorine Atoms	PCDD Positional Isomer		PCDF Positional Isomer	
	First Eluter	Last Eluter	First Eluter	Last Eluter
4[a]	1,3,6,8	1,2,8,9	1,3,6,8	1,2,8,9
5	1,2,4,6,8/	1,2,3,8,9	1,3,4,6,8	1,2,3,8,9
1,2,4,7,9				
6	1,2,4,6,7,9/	1,2,3,4,6,7	1,2,3,4,6,8	1,2,3,4,8,9
1,2,4,6,8,9				
7	1,2,3,4,6,7,9	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,7,8,9
8	1,2,3,4,6,7,8,9	1,2,3,4,6,7,8,9		

(a) In addition to these two TCDD isomers, the 1,2,3,4-, 1,2,3,7-, 1,2,3,8-, 2,3,7,8-, $^{13}C_{12}$-2,3,7,8- and 1,2,3,9-TCDD isomers must also be present as a check of column resolution.

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

(a) Used only for ^{13}C-HxCDF (IS)
(b) Used only for ^{13}C-HpCDF (IS)

2,3,7,8-TCDD Equivalency Factors (TEFs) for the Polychlorinated Dibenzodioxins and Dibenzofurans

Number	Compound(s)	TEF[a]
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,4,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

(a) Taken from "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxin and -Dibenzofurans (CDDs and CDFs) and 1989 Update", (EPA/625/3-89/016, March 1989).

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDF
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDF
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDF (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	TCDF
	[354.9792]	LOCK	C_9F_{13}	TCDF
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8250	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	423.7767	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7780	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[442.9728]	LOCK	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:

H	=	1.007825	0	=	15.994915

C	=	12.000000	^{35}Cl	=	34.968853
^{13}C	=	13.003355	^{37}Cl	=	36.965903
F	=	18.9984			

S = internal/recovery standard

1.0 DATA COMPLETENESS FOR DIOXIN/DIBENZOFURAN ANALYSIS IN AIR

Validation worksheets are applicable to USEPA Method TO-9.
Data validation guidelines:

- USEPA. 1994 *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS),* Albany, New York.
- U.S. Environmental Protection Agency (USEPA) Region V. 1997. *Standard Operating Procedure for Validation of CLP Organic Data.* Chicago, Illinois

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss any special notes regarding problems with sample receipt, condition of samples, analytical problems, or special notations affecting the quality of PCDD/PCDF data as documented by the laboratory in the case file or narrative. (If desired, attach copy of case narrative).

1.2 Do the detection limits listed on the sample report match those listed in the QAPP?

1.3 Were the correct units indicated, mg/m^3 or total µg per PUF for air?

1.4 Were samples iced for sample shipment?

ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.5 Were raw data to support analyses and QC operations present and complete?

ACTIONS: If no, for any of the above, contact the laboratory for an explanation. If missing data cannot be provided, use professional judgement in qualifying data. Review all problems and resolutions regarding data completeness in final report.

1.6 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing raw data or applicable QC forms etc).

1.7 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

Criteria:

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Holding times for PCDD/PCDF:
Air samples – 7 days from collection to extraction and 40 days from extraction to analysis.

The holding times for extraction/preparation presented in Method 8290 are considered to be contractual holding times only. There are no demonstrated maximum holding times associated with the extraction/preparation of PCDDs/PCDFs in aqueous, solid, semi-solid, tissues, and other sample matrices. If samples are stored properly. the holding times for extraction/preparation are up to one year. Sample extracts are to be analyzed within 45 days of preparation.

VALIDATION ACTION:
If holding times for analysis of sample extracts are exceeded, positive results and detection limits are considered to be approximate (UJ, J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 INSTRUMENT PERFORMANCE (MASS CALIBRATION, GC COLUMN PEFORMANCE CHECK

Criteria:

Mass calibration

Mass calibration of the MS must be performed prior to analyzing calibration solutions, Blanks, samples, and QC samples. The mass spectrometer must be operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. A minimum required resolving power of 10000 is obtained for perfluorokerosene (PFK) ion 380.9760. This is done by first measuring peak width at 5% of the maximum. This should not exceed 100 ppm, i.e., it should not exceed 0.038, for ion 380.9760. Resolving power, then is calculated using the formula,

$$\text{Resolving Power} = m/\ m = 380.9760/0.038 = 10025.$$

The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less. At a minimum, the ions listed in the method for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all descriptors contain 10 ions. The selection of the molecular ions M and M+2 for ^{13}C-HxCDF and ^{13}C-HpCDF rather than M+2 and M+4 (for consistency) was made to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extract analyses. The selection of the lock-mass ion is left to the performing laboratory.

The recommended mass spectrometer tuning conditions are based on the groups of monitored ions shown in the method. By using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors.

Static resolving checks must be performed at the beginning and at the end of each 12-hour shift. Raw data printouts of the mass resolving checks analyzed at the beginning and end of the 12-hour shift must be included in the data package. The injection time for the beginning mass resolution check that the laboratory submits as documentation of compliant instrument performance is considered to be the beginning of the 12-hour shift.

Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, it is recommended to select a lock-mass ion from the reference compound (PFK is recommended) used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. An acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. The level of the reference compound (PFK) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10 percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

3.1 Was mass calibration performed at the frequency given above?

3.2 Was the resolving power of PFK ion 380.9760 above 10000, when it was transmitted at the accelerating voltage corresponding to m/z ion 304.9824?

VALIDATION ACTION:
Qualify associated positive sample results and detection limits as approximate (UJ,J).

GC Column Performance Check Solution
The GC Column Performance Check solution must contain the first and the last isomers of each homologue PCDD/PCDF, (the internal and recovery standards are optional). The solution also should contain a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. All peaks must be labeled and identified on the Selected Ion Current Profiles (SICPs). In addition, the first and last eluters must be labeled with the letter F or L, as appropriate. The chromatographic separation between 2378-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of < 25%.

At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 shall be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check shall also be performed to demonstrate adequate mass resolution using an appropriate reference compound.

Switching Times – Allowable tolerance on the daily verification with the GC performance check solution should be better than 10 seconds for the absolute retention times of all the components of the mixture. Particular caution should be exercised for the switching time between the last tetrachlorinated congener (i.e., 1,2,8,9-TCDD) and the first pentachlorinated congener (i.e., 1,3,4,6,8-PeCDF), as these two compounds elute within 15 seconds of each other on the 60 m DB-5 column.

3.3 For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of GC column performance check solution at the beginning of every 12 hour period. Was this performed accordingly?

VALIDATION ACTION: If the GC column performance check solution was not analyzed at the required frequency,
qualify associated positive sample results and detection limits as approximate (UJ,J).

3.4 Were all peaks labeled and identified on the Selected Ion Current Profiles (SICPs)?___

VALIDATION ACTION:
Request corrected data from laboratory.

3.5 For DB-5 or equivalent, the peak separation between the unlabeled 2378-TCDD and the peaks representing any other TCDD isomer shall be resolved with a valley of < 25 percent. Was this criteria met?

Calculation: % Valley = (x/y) x (100)

Y = The peak height of 2,3,7,8-TCDD isomer

X = The distance from the baseline to the bottom of the valley between the adjacent peaks.

VALIDATION ACTION: If the percent valley criteria are not met, qualify all positive data J. Do not qualify detection limits.

3.6 Is the last eluting tetra chlorinated congener (1,2,8,9-TCDD) and the first eluting penta chlorinated congener (1,3,4,6,8-PeCDF) separated properly, since they elute within 15 seconds of each other?

VALIDATION ACTION: If one of the congener is missing, document in the validation report.

3.7 List below the samples qualified due to mass calibration or GC column performance excursions.

Mass resolution check ID	Excursion	Samples Affected (client/lab ID)	Action

4.0 INITIAL CALIBRATION

Criteria:

The initial calibration standard solutions (HRCC1-HRCC5) must be analyzed prior to any sample analysis. They do not have to be analyzed daily, provided the continuing calibration standard met all criteria. However, initial calibration should be analyzed at least once every week and/or whenever the continuing calibration standard does not meet all criteria. The calibration standards must be analyzed on the same instrument using the same GC/MS conditions that were used to analyze the GC column performance check solution.
The total cycle time must be < 1 second (includes the sum of all the dwell times and voltage reset times).
The chromatographic resolution between the 2378-TCDD and the peaks representing any other unlabeled TCDD isomers must be resolved with a valley of < 25 percent.
In the HRCC3 solution, the chromatographic peak separation between 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD shall be resolved with a valley of < 50 percent.
For all calibration solutions the retention times of the isomers must fall within the retention time windows established by the GC column performance check solution. In addition, the absolute retention times of recovery standards, 13C121234-TCDD and 13C12-123789HxCDD shall not change by more than 10 seconds between the HRCC3 analysis and the analysis of any other standard.
The two SIM ions for each homolog must maximize simultaneously and within 3 seconds of the corresponding labeled isomer ions.
The relative ion abundance criteria for PCDDs/PCDFs must be met.
The relative ion abundance criteria for the labeled internal and recovery standards must be met.
For all calibration solutions, including HRCC3, the signal to noise ratio (S/N) for the GC signal present in every SICP, including the ones for the labeled standards must be > 10.
The percent relative standard deviations (% RSD) for the mean response factors (RRF) from the 17 unlabeled standards must not exceed + 20%, and those for the nine labeled reference compounds must not exceed + 30%.

Was the initial calibration performed at the frequency specified above?

Is mass calibration performed as described previously?

Is the total cycle time < 1 second?

Were SIM data acquired for each of the ions, including interfering ions?

Ions Monitored for HRGC/HRMS Analysis of PCDDs/PCDFs

Descriptor	Accurate[a] Mass	Ion ID	Elemental Composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	${}^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	${}^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDF
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDF
	331.9368	M	${}^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDF (S)
	333.9338	M+2	${}^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	TCDF
	[354.9792]	LOCK	C_9F_{13}	TCDF
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	${}^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	${}^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	${}^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	${}^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
	[354.9792]	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	${}^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	${}^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	${}^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	${}^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7788	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8250	M	${}^{13}C_{12}H{}^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	${}^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	423.7767	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	${}^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	${}^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCDPE
	[430.9728]	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7780	M+2	${}^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	${}^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE
	[442.9728]	LOCK	$C_{10}F_{17}$	PFK

(b) The following nuclidic masses were used:

H	=	1.007825	0	=	15.994915
C	=	12.000000	^{35}Cl	=	34.968853
^{13}C	=	13.003355	^{37}Cl	=	36.965903
F	=	18.9984			

S = internal/recovery standard

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

(c) Used only for ^{13}C-HxCDF (IS)
(d) Used only for ^{13}C-HpCDF (IS)

VALIDATION ACTION:

1. If the 25% percent valley for TCDD and 50%valley for HxCDD requirement are not met, quality positive data (J). Do not qualify non-detects. The tetra, pentas and hexas (dioxins and furans) are affected. Heptas and Octas are not affected.
2. If the %RSD for each unlabeled isomer exceeds 20%,or the %RSD for each labeled isomer exceeds 30%, flag the associated sample positive results for that specific isomer as estimated ("J"). No effect on the non-detect data.
3. If the ion abundance ratio for an analyte is outside the limits, reject the results for that analyte (R).
4. If the ion abundance ratio for an internal or recovery standard falls outside the QC limits flag the associated positive hits with J. No effect on the non-detects.
5. If the signal to noise ratio (S/N) is below control limits, use professional judgement to determine quality of the data.
6. If the selected monitoring ions were not used for data acquisition, the lab must be asked for an explanation. If an incorrect ion was used, reject all the associated data.
7. If mass calibration criteria as previously described is not met, specify that in case narrative.
8. Non compliance of all other criteria specified above should be evaluated using professional judgement.

Spot check response factor calculations and ion ratios.
Ensure that the correct quantitation ions for the unlabeled PCDDs/PCDFs and internal standards were used.
Verify that the appropriate internal standard was used for each isomer.

To recalculate the response factor, use the equation:

$$RRFn = [(An^1 + An^2) \times Qis] / [(Ais^1 + Ais^2) \times Qn]$$

$$RRFis = [(Ais^1 + Ais^2) \times Qrs] / [(Ars^1 + Ars^2) \times Qis]$$

Where:

An^1 and An^2 = integrated areas of the two quantitation ions of isomer of interest.
Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.
Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.
Qn = quantity of the unlabeled PCDD/PCDF analyte injected (pg)
Qis = quantity of the appropriate internal standard injected (pg)
Qrs = quantity of the appropriate recovery standard injected (pg)

List below all initial calibrations and samples qualified due to initial calibration excursions.

Unique IC ID	Excursion	Samples Affected	Action

5.0 CONTINUING CALIBRATION

Criteria:

The continuing calibration must be performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A continuing calibration is also required at the end of a 12 hour shift.
The total cycle time is < 1 second.
SIM data are acquired for each of the ions including diphenylether interfering ions.
For the continuing calibration solution the retention time of the isomers must fall within the retention time windows established by the GC column performance check solution.
The absolute retention time of the recovery standards 13C121234-TCDD and 13C12123679-HxCDD shall not change by more than 10 seconds between the initial HRCC3 and ending HRCC3 standard analyses.
The two SIM ions for each homolog must maximize simultaneously (+ 2 sec) and within 3 seconds of the corresponding ions of the labeled isomers.
For the HRCC3 standard solution, the signal to noise ratio (S/N) for the unlabeled PCDD/PCDF ion shall be greater than 2.5.
For the internal standards and the recovery standards, the signal to noise ratio (S/N) shall be greater than 10.
The relative ion abundance criteria for all PCDD/PCDF shall be met.
The relative ion abundance criteria for all internal and recovery standards must be met.
The %Difference of RRF of each unlabeled analyte must be within +20 percent of the mean RRF established during the initial calibration. The measured RRFs for each of the labeled standards must be within + 30 percent of the mean RRF established during the initial calibration.

Was the same internal standard used to calculate RRF for each PCDD/PCDF homolog in the initial calibration?

Was the chromatographic peak separation on DB-5 (or equivalent) column between unlabeled 2378-TCDD and the peaks representing any other unlabeled TCDD isomers resolved with a valley of < 25 percent?

Was the chromatographic peak separation between the 123478-HxCDD and the 123678-HxCDD in the HRCC3 solution resolved with a valley of <50 percent?

Was the continuing calibration run at the required frequency?

VALIDATION ACTION:

1. If any of the requirements for total cycle time <1 second, SIM data acquired for each ion (including diphenylether), retention times for continuing calibration solution falling within windows, retention times for recovery standards (not changing more than 10 seconds), and using the same internal standard as in the initial calibration are not met, use professional judgement to determine the validity of the data.

2. If any requirements listed for ions maximizing within 2-3 seconds, S/N ratio in the HRCC3 standard, internal standards and recovery standards, relative ion abundance criteria for analytes, internal standards, and recovery standards are not met reject all data (R) directly affected by each specific problem.

3. When the %D of the RRF is in between 30% and 50%, all the data for the outlier congeners are flagged (J). Data with %D above 50% are rejected (R).

4. If the continuing calibration standard was not analyzed at the required frequency, reject all the data (R). Contact Project Manager to initiate re-collection.

5. If the 25 percent valley and 50 percent valley criteria are not met, qualify all positive data with (J). Do not qualify non-detects. The tetras, pentas and hexas (dioxins and furans) are affected. Heptas and octas are not affected. If the percent valley is >75 percent and 2378-TCDD is non-detect but 1234-TCDD or an adjacent TCDD isomer is present, the data is questionable. The sample must be reanalyzed. Contact Project Manager. If the valley criteria for HxCDD are not met, but the valley criteria for TCDD are met or vice-versa, use professional judgement to determine which data must be qualified.

6. If the HRCC3 standard performed at the end of the 12 hour shift did not meet criteria specified in retention times of the isomers, S/N ratio in the HRCC3 standard, internal standards and recovery standards, relative ion abundance criteria for analytes, internal standards, and recovery standards, examine the samples which were analyzed prior to this standard and use professional judgement to determine if data qualification is necessary.

7.0 For all other criteria, use professional judgement.

Spot check response factor calculations and ion ratios. Verify that the appropriate quantitation ions for the unlabeled PCDD/PCDFs and internal standards were used.

To recalculate RRFs for the unlabeled target analytes, and the RRFs for the nine labeled internal standards, use the following equations:

$RRFn = [(An^1 + An^2) \times Qis] / [(Ais^1 + Ais^2) \times Qn]$
$RRFis = (Ais^1 + Ais^2) \times Qrs \ / \ [(Ars^1 + Ars^2) \times Qis]$
Where:
An^1 and An^2 = integrated areas of the two quantitation ions of isomer of interest.
Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.
Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.
Qn = quantity of the unlabeled PCDD/PCDF analyte injected (pg)
Qis = quantity of the appropriate internal standard injected (pg)
Qrs = quantity of the appropriate recovery standard injected (pg)

To calculate percent difference use the following equation:
% Difference = [(RRFi - RRFc) x 100] /[RRFi]

Where:
RRFi = Relative response factor established during initial calibration
RRFc = Relative response factor established during continuing calibration

5.1 List below all continuing calibrations and samples qualified due to continuing calibration excursions.

Unique CC ID	Compound	Excursion	Action	Samples Affected (client, lab IDs)

6.0 SAMPLE DATA (IDENTIFICATION)

Criteria:

Were the following MS/DS conditions used?

The total cycle time was < 1 second.
SIM data were acquired for each of the ions including diphenylether interfering ions.

Were the following identification criteria met?

For the 2378 substituted isomers found present and for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard.

For the 2378 substituted isomer reported present, and for which a labeled standard does not exist, the relative time (RRT) of the analyte must be within +.005 RRT units of the RRT established by the continuing calibration standard (HRCC3).

For non-2378 substituted compounds (tetra through octa) found present, the retention time must be within the window established by the GC column performance check solution, for the corresponding homologue.

All specified ions for each PCDD/PCDF isomer and the labeled standards must be present in the SICP. The two SIM ions for the analyte, the internal standards and recovery standards must maximize simultaneously (+2 seconds).

The integrated ion current for each characteristic ion of the analyte identified as positive, must be at least 2.5 times background noise and must not have saturated the detector.

The integrated ion current for the internal and recovery standard characteristic ions must be at least 10 times background noise.

The relative ion abundance criteria for all PCDDs/PCDFs found present must be met.

The relative ion abundance criteria for the internal and recovery standards must be met.

The identification of a GC peak as a PCDF can only be made if no signal having a S/N > 2.5 is detected at the same time in the corresponding polychlorinated diphenyl ether channel.
Is the above condition met?

VALIDATION ACTION:
1. Reject (R) all positive data for the analytes which do not meet criteria for retention times for 2378 substituted isomers and non-2378 substituted isomers, and the presence of all ions for each isomer labeled standards in the SICP.

2. If the criteria for the integrated ion current for each ion for the analytes being 2.5 times the background noise are not met but all other criteria are met, qualify all positive data of the specific analyte with J.

3. If the requirements for the integrated ion current for the internal and recovery standard ions being 10 times the background noise are not met but all other requirements are met qualify the positive data of the corresponding analytes as approximate (J).

4. If the analytes reported positive do not meet ion abundance criteria for analytes, reject (R) all positive data for these analytes. Change the positive values to EMPC (estimated maximum possible concentration).

5. If the internal standards and recovery standards do not meet ion abundance criteria but they meet all other criteria flag all corresponding data with "J".

6. If PCDF is detected but an interfering PCDPE is also detected reject the PCDF data (R). The reported value of PCDF is changed to EMPC.

7. If the lab did not monitor for PCDPEs, qualify all positive furan data as approximate (J).

Spot check calculations for positive data and verify that the same internal standards used to calculate RRFs were used to calculate concentration and EMPC. Ensure that the proper PCDDs/PCDFs and internal standards were used.

To recalculate the concentration of individual PCDD/PCDF isomers in the sample use the following equation:

AIR

$$Cn\ (ng/L) = [Qis \times (An^1 + An^2)]/[V \times (Ais^1 + Ais^2) \times RRFn]$$

Where:
An^1 and An^2 = integrated ion abundances (peak areas) of the quantitation ions of the isomer of interest.
Ais^1 and Ais^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard.
V= Volume (ml) of air extracted (m^3)
Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction
RRFn= Calculated relative response factor from continuing calibration.

6.1 List samples qualified due to identification excursions.

Sample ID (client/lab)	Compound	Excursion	Action

7.0 ESTIMATED DETECTION LIMITS (EDL)

Criteria:

The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EDL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

Samples giving a response for both quantitation ions that is less than 2.5 times the background level.

Use the expression for EDL to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions. of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that peak height.

Was an EDL calculated for each 2,3,7,8-substituted isomer that was not identified regardless of whether other non-2378 substituted isomers were present?

Use the equation below to check EDL calculations:

AIR

$$\text{EDL (pg/m}^3) = [2.5 \text{ x Qis x } (Hx^1 + Hx^2)]/[V \text{ x } (His^1 + His^2) \text{ x RRFn}]$$

Where:

Hx^1 and Hx^2 = peak heights of the noise for both quantitation ions of the 2,3,7,8-substituted isomer of interest.

His^1 and His^2 = peak heights of both the quantitation ions of the appropriate internal standards.

Where:

V= Volume (ml) of air extracted (m^3)

Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction

RRFn= Calculated relative response factor from continuing calibration.

VALIDATION ACTION:

Check the EDL data to verify that peak heights and not areas were used for this calculation. If the area algorithm was used, the validator should contact the laboratory for recalculation. The Project Manager must be notified.

8.0 ESTIMATED MAXIMUM POSSIBLE CONCENTRATION (EMPC)

Criteria:
When the response of a signal having the same retention time as a 2,3,7,8-substituted congener has a S/N in excess of 2.5 and does not meet any of the other qualitative identification criteria, calculate the "**Estimated Maximum Possible Concentration**" (EMPC).

Was an EMPC calculated for 2378-substituted isomers that had S/N ratio for the quantitation and confirmation ions greater than 2.5, but did not meet all the identification criteria?

Use the equation below to check EMPC calculations:

AIR
EMPC (pg/m^3) = $[(Ax^1 + Ax^2) \times Qis \times D]/[(Ais^1 + Ais^2) \times RRFn \times V]$

Where:
Ax1 and Ax2 = areas of both quantitation ions.
Ais^1 and Ais^2 = integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard.
V= Volume (ml) of air (m^3)
Qis= Quantity (pg) of the appropriate internal standard added to the sample prior to extraction
RRFn= Calculated relative response factor from continuing calibration.
D is dilution factor.

VALIDATION ACTION:

1. If EDL or EMPC of an analyte which was not reported as present is missing, contact the laboratory for correction.

2. If the spot check calculations yielded EDLs or EMPCs different from those reported in Form I, contact the laboratory for an explanation.

3. If EDLs or EMPCs for the most toxic analytes (TEF> 0.05) are above CRQLs contact TPO for sample re-collection.

Check EMPC calculation.

9.0 BLANK ANALYSIS (METHOD, RINSATE, FIELD)

Note for Region V: Equipment/Field blanks are not used for qualification of samples.

Field Blank—consists of a sample cartridge containing PUF and filter that is spiked with the filed fortification solution, shipped to the field, installed on the sampler, and passively exposed at the sampling area (the sampler is not operated). It is then sealed and returned to the laboratory for extraction, cleanup, and HRGC-HRMS analysis. It is treated in exactly the same manner as a test sample. A field blank is processed with each sampling episode. The field blank represents the background contributions from passive exposure to ambient air, PUF, quartz fiber filter, glassware, and solvents.

Laboratory Method Blank—represents the background contributions from glassware, extraction and cleanup solvents. A Soxhlet extractor is spiked with a solution of 13C12 -labeled internal standards, extracted, cleaned up, and analyzed by HRGC-HRMS in exactly the same manner as the test samples.
The method blank should be free of interferences that affect the identification and quantification of PHDDs and PHDFs. A valid method blank is an analysis in which all internal standard signals are characterized by S/N ratio greater than 10:1 and the MDLs are adequate for the study. The set of samples must be extracted and analyzed again if a valid method blank cannot be achieved.

Solvent Blank—an aliquot of solvent (the amount used in the method) that is spiked with the 13C12 -labeled internal standards and concentrated to 60 µL for HRGC-HRMS analysis. The analysis provides the background contributions from the specific solvent. An acceptable solvent blank analysis (free of PHDDs/PHDFs) should be achieved before continuing with analysis of the test samples.

Method Blank

Criteria:
Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?

Acceptable method blanks must should be free of interferences that affect the identification and quantification of PHDDs and PHDFs.
Is this criteria met?

VALIDATION ACTION:
1. If the proper number of method blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the method blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD, 12378PeCDF or 23478 PeCDF at a concentration higher than the upper MCL, reject all contaminant compound positive data for the associated samples (R) and contact the Project Manager to initiate re-collection if it is deemed necessary.

3. If the method blank is contaminated with any of the above isomers at a concentration of less than the upper MCL specified in the method or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

Rinsate Blank

Criteria:

One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent. Was rinsate blanks collected at the above frequency?

Do any rinsate blanks show the presence of 2378-TCDD, 2378-TCDF, and 12378PeCDD at amounts > .5 ug/L or any other analyte at levels > 1 ug/L?

VALIDATION ACTION:
1. If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the Project Manager to discuss what proper action must be taken.

Field Blanks/Solvent Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

Criteria:

The field blanks are blind blanks at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

Were the following conditions met?

Acceptable field blanks must not contain any signal of 2378-TCDD, 2378-TCDF, 12378-PeCDD and 12378-PeCDF equivalent to a concentration of > 20 ppt.

For other 2378 substituted PCDD/PCDF isomers of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method.

VALIDATION ACTION:

When the field blank/solvent blank is found to be contaminated with target compounds, apply the same action as described for the method blank.
1. If the proper number of blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD, 12378PeCDF or 23478 PeCDF at a concentration higher than the upper MCL, reject all contaminant compound positive data for the associated samples (R) and contact the Project Manager to initiate re-collection if it is deemed necessary.

3. If the blank is contaminated with any of the above isomers at a concentration of less than the upper MCL specified in the method or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

9.1 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

10.0 INTERNAL STANDARDS EVALUATION

Criteria:

For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

1 Were the samples spiked with all the internal standards listed in the method?

2 Were internal standard recoveries within the required (40 - 135%) limits?

.3 If not, were samples reanalyzed?

VALIDATION ACTION:

1. If the internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.
2. If the internal standard recovery is above the upper limit (135 percent) flag all associated data (positive and non-detect data) with "J".
3. If the internal standard recovery is less than 10%, qualify all associated data reject (R) when highly toxic isomers (TEF> 0.05) are affected, notify Project Manager to initiate re-collection.

Recalculate the percent recovery for internal standards in the sample extract, Ris, using the formula:

$$Ris = [(Ais^1 + Ais^2) \times Qrs \times 100\%] / [(Ars^1 + Ars^2) \times RRFis \times Qis]$$

Where:

Ais^1 and Ais^2 = integrated areas of the two quantitation ions of the appropriate internal standard.
Ars^1 and Ars^2 = integrated areas of the two quantitation ions of the appropriate recovery standard.
Qis = quantity of the appropriate internal standard injected (pg)
Qrs = quantity of the appropriate recovery standard injected (pg)
RRFn= Calculated relative response factor from continuing calibration.

10.1 List samples qualified due to internal standard excursions.

Instrument:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Action

11.0 RECOVERY STANDARDS

Criteria:
There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration?
Area upper limit= +100% of recovery standard area.
Area lower limit= -50% of recovery standard area.

Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?

VALIDATION ACTION:

1. If the recovery standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, reject all associated non-detect data (R) and flag the positive data (J).

3. If the retention time of the recovery standard differs by more than 10 seconds from the daily calibration use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the GC column performance check solution.

11.1 List samples qualified due to recovery standard excursions.

Instrument:

Sample ID (client/lab ID)	Recovery Standard	Area and Percent Recovery	Action

12.0 MATRIX SPIKE

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

Criteria:

The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?

.2 Was the percent recovery of 2378-TCDD and other 2378-substituted PCDDs/PCDFs within 50 to 150 percent?

VALIDATION ACTIONS:

If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 50-150% limits of the matrix spike data may be used to flag data of the spiked sample only.

12.1 List samples qualified due to matrix spike excursions.

Instrument:

Matrix Spike ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

13.0 DUPLICATE SAMPLES

Criteria:
The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean).

For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency?

Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8 substituted isomers and 50% for the rest of the congeners?

VALIDATION ACTION:
The duplicate results must be used in conjunction of other QC data. If no hits are reported, precision may be assessed from the internal standard recoveries.

13.1 List samples qualified due to duplicate excursions.

Instrument:

Duplicate ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

14.0 SECOND COLUMN CONFIRMATION

Note:
For Air Samples, only one analysis is possible per sample.

15.0 SAMPLE REANALYSIS

Note For Air Samples, Only One Analysis Is Possible.

16.0 TOXICITY EQUIVALENCY FACTOR (TEF)

Criteria:

The 2,3,7,8-TCDD **toxicity equivalents** (TE) of PCDDs and PCDFs present in the sample are calculated. This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDD and PCDFs and to OCDD and OCDF. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds.

When calculating the 2378-TCDD Toxicity Equivalency of a sample only those 2378 substituted isomers that were positively identified in the sample must be included in the calculations. The sum of the TEF adjusted concentration is used to determine when a second column confirmation is required to achieve isomer specificity.

Did the lab include EMPC or EDL values in the toxicity equivalency calculations?

VALIDATION ACTION:

1. If the toxicity equivalency calculations were not performed properly notify TPO.

2. If the toxicity equivalency exceeded the required limits (0.7 ppb for soil/sediment, 7ppt for aqueous and 7ppb for chemical waste samples), notify the Project Manager.

16.1 List samples affected by TEF excursions.

INSTRUMENT:

Sample ID	Analyte	Excursion	Action

17.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

17.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?

Summarize below compounds that did not meet above criteria.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

ADDITIONAL NOTES:

O'Brien & Gere Engineers Data Validation Form

USEPA Method TO-9 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) In Air (8290)

Date:____________________ Number of samples and compounds per sample:________________

Project Number:____

Validator:____Equipment Blanks:________

Project: ____Blind/Field Duplicates:______

Laboratory:____MS/MSDs:_______________

QAPP:____________________________________ DV Guidelines: USEPA Region II

Laboratory package number:__________________PARTIAL VALIDATION

Method references:

- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-9A Determination of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans In Ambient Air.* Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, 3rd Edition. Washington D.C.*

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-9	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

CT	Sample ID	Date collected 1999 2000	Date received 1999 2000	Method TO-9	M	Laboratory ID	P N
Note: CT indicates cooler temperature; M indicates matrix; PN indicates laboratory package number or SDG number							

Sample ID	QC Batch

USABILITY SUMMARY:

Number of samples * number of compounds per sample = total analyses in project
Percent rejected = total rejected analyses/total analyses in project
Percent Usability = Usable analyses (total analyses – rejected) / total analyses in project

Sample Type	Type of Excursion – Data Rejection	Total number of samples in packages	Number of affected samples	Number of compounds per sample	Total rejected analyses	Percent Rejected	Percent Usability

Data Validation Forms
Method TO-9 Polychlorinated Dibenzodioxin and Dibenzofurans (PCDD/PCDFs) in Air (8290)

The following worksheets are based on:

- USEPA. 1999 *USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Compendium Method TO-9A Determination of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans In Ambient Air*, Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio.
- USEPA. 1994 *USEPA Region II Data Validation SOP For SW-846 Method 8290 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) By High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)*, Albany, New York.
- U.S. Environmental Protection Agency (USEPA). 1996. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd Edition. Washington D.C.*

Table of Contents:

VALIDATION DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the qualifiers assigned to results in the data validation process.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

U - Not detected above the reported detection limit.

NJ - There is presumptive evidence for the presence of the compound at an estimated value.

Note To Data Validators:

The following procedure should be followed when using these forms:

1. Fill out forms completely; **for partial validation, raw data is Not Reviewed.**
2. Use specific and unique identifications when identifying QC samples for documenting in the data validation report.
3. Reference both client and laboratory identifications on the forms for cross checking purposes.
4. Indicate bias when possible (↑↓).
5. Qualify associated sample result sheets clearly in ink under column marked QUAL.
6. Note that, due to possible rounding discrepancies, allow recoveries to fail criteria by 1% outside the control limits.

1.0 DATA COMPLETENESS FOR DIOXIN/DIBENZOFURAN ANALYSIS IN AIR

1.1 Traffic Report or Lab Narrative Notes: Briefly discuss issues with sample receipt or condition of samples.

1.2 Were samples iced for sample shipment?
ACTION: If samples were not iced or the ice was melted upon arrival at the laboratory and the cooler temperature was elevated (> 10° C), then note in the validation report.

1.3 List below any communication with laboratory regarding problems with data completeness, with reference to data, contact person, specific problems and resolutions (This would include missing QC forms).

1.4 Were equipment blanks, MS/MSD, field duplicate samples analyzed at the correct frequency as listed in the QAPP?

2.0 HOLDING TIMES

Criteria:

The objective is to ascertain the validity of the analytical results based on the holding time of the sample from the time of collection to the time of analysis.

2.1 Holding times for PCDD/PCDF:
Air samples – 7 days from collection to extraction and 40 days from extraction to analysis.

The holding times for extraction/preparation presented in Method 8290 are considered to be contractual holding times only. There are no demonstrated maximum holding times associated with the extraction/preparation of

PCDDs/PCDFs in aqueous, solid, semi-solid, tissues, and other sample matrices. If samples are stored properly, the holding times for extraction/preparation are up to one year. Sample extracts are to be analyzed within 45 days of preparation.

VALIDATION ACTION:
If holding times for analysis of sample extracts are exceeded, positive results and detection limits are considered to be approximate (UJ, J).

2.2 Summarize below the samples qualified due to holding time excursions.

Sample ID (client/lab)	Date Collected	Date Extracted	Date Analyzed	Action (number of days out and qualifier)

3.0 BLANK ANALYSIS (METHOD, RINSATE, FIELD)

Note for Region V: Equipment/Field blanks are not used for qualification of samples.

Field Blank—consists of a sample cartridge containing PUF and filter that is spiked with the filed fortification solution, shipped to the field, installed on the sampler, and passively exposed at the sampling area (the sampler is not operated). It is then sealed and returned to the laboratory for extraction, cleanup, and HRGC-HRMS analysis. It is treated in exactly the same manner as a test sample. A field blank is processed with each sampling episode. The field blank represents the background contributions from passive exposure to ambient air, PUF, quartz fiber filter, glassware, and solvents.

Laboratory Method Blank—represents the background contributions from glassware, extraction and cleanup solvents. A Soxhlet extractor is spiked with a solution of 13C12 -labeled internal standards, extracted, cleaned up, and analyzed by HRGC-HRMS in exactly the same manner as the test samples.
The method blank should be free of interferences that affect the identification and quantification of PHDDs and PHDFs. A valid method blank is an analysis in which all internal standard signals are characterized by S/N ratio greater than 10:1 and the MDLs are adequate for the study. The set of samples must be extracted and analyzed again if a valid method blank cannot be achieved.

Solvent Blank—an aliquot of solvent (the amount used in the method) that is spiked with the 13C12 -labeled internal standards and concentrated to 60 µL for HRGC-HRMS analysis. The analysis provides the background contributions from the specific solvent. An acceptable solvent blank analysis (free of PHDDs/PHDFs) should be achieved before continuing with analysis of the test samples.

Method Blank

Criteria:

Has a method blank per matrix been extracted and analyzed with each batch of 20 samples?

Acceptable method blanks must should be free of interferences that affect the identification and quantification of PHDDs and PHDFs.
Is this criteria met?

VALIDATION ACTION:

1. If the proper number of method blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the method blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD, 12378PeCDF or 23478 PeCDF at a concentration higher than the upper MCL, reject all contaminant compound positive data for the associated samples (R) and contact the Project Manager to initiate re-collection if it is deemed necessary.

3. If the method blank is contaminated with any of the above isomers at a concentration of less than the upper MCL specified in the method or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

Rinsate Blank

Criteria:

One rinsate blank must be collected for each batch of 20 soil samples or one per day whichever is more frequent. Was rinsate blanks collected at the above frequency?

Do any rinsate blanks show the presence of 2378-TCDD, 2378-TCDF, and 12378PeCDD at amounts > .5 ug/L or any other analyte at levels > 1 ug/L?

VALIDATION ACTION:
1. If any rinsate blank was found to be contaminated with any of the PCDDs/PCDFs notify the Project Manager to discuss what proper action must be taken.

Field Blanks/Solvent Blanks
Note for Region V: Equipment/Field blanks are not used for qualification of samples.

Criteria:

The field blanks are blind blanks at the frequency of one field blank per 20 samples or one per samples collected over a period of one week, which ever comes first. A typical "field blank" will consist of uncontaminated soil. The field blanks are used to monitor possible cross contamination of samples in the field and in the laboratory.

Were the following conditions met?

Acceptable field blanks must not contain any signal of 2378-TCDD, 2378-TCDF, 12378-PeCDD and 12378-PeCDF equivalent to a concentration of > 20 ppt.

For other 2378 substituted PCDD/PCDF isomers of each homologue the allowable concentration in the field blank is less than the upper MCLs listed in the method.

VALIDATION ACTION:

When the field blank/solvent blank is found to be contaminated with target compounds, apply the same action as described for the method blank.
1. If the proper number of blanks were not analyzed, notify the Project Manager. If they are unavailable, reject (R) all positive sample data. However, the reviewer may also use professional judgement to accept or reject positive sample data if no blank was run.

2. If the blank is contaminated with 2378-TCDD, 2378-TCDF, 12378PeCDD, 12378PeCDF or 23478 PeCDF at a concentration higher than the upper MCL, reject all contaminant compound positive data for the associated samples (R) and contact the Project Manager to initiate re-collection if it is deemed necessary.

3. If the blank is contaminated with any of the above isomers at a concentration of less than the upper MCL specified in the method or of any other 2378-substituted isomer at any concentration and the concentration in the sample is less than five times the concentration in the blank, transfer the sample results to the EMPC/EDL column and cross-out the value in the concentration column. If the concentration in the sample is higher than five times the concentration in the blank, do not take any action.

3.1 List all blanks and samples qualified due to blank contamination.

Unique Blank Identification	Compound	Concentration	Action Level	Samples Affected (client/lab ID) and Action

4.0 INTERNAL STANDARDS EVALUATION

Criteria:

For each sample, method blank and rinsate, calculate the percent recovery. The percent recovery should be between 40 percent and 135 percent for all 2,3,7,8-substituted internal standards.

1 Were the samples spiked with all the internal standards listed in the method?

2 Were internal standard recoveries within the required (40 - 135%) limits?

.3 If not, were samples reanalyzed?

VALIDATION ACTION:

1. If the internal standard recovery was below 25 percent, reject (R) all associated non-detect data (EMPC/EDL) and flag with "J" all positive data.
2. If the internal standard recovery is above the upper limit (135 percent) flag all associated data (positive and non-detect data) with "J".
3. If the internal standard recovery is less than 10%, qualify all associated data reject (R) when highly toxic isomers (TEF> 0.05) are affected, notify Project Manager to initiate re-collection.

4.1 List samples qualified due to internal standard excursions.

IINSTRUMENT:

Sample ID (client/lab ID)	Internal Standard	Area and Percent Recovery	Action

5.0 RECOVERY STANDARDS

For partial validation, recovery standards are reviewed if summary forms are provided by the laboratory.

Criteria:
There are no contractual criteria for the Recovery Standard area. However, because it is very critical in determining instrument sensitivity, the Recovery Standard area must be checked for every sample.

Are the recovery standard areas for every sample and blank within the upper and lower limits of each associated continuing calibration?
Area upper limit= +100% of recovery standard area.
Area lower limit= -50% of recovery standard area.

Is the retention time of each recovery standard within 10 seconds of the associated daily calibration standard?

VALIDATION ACTION:

1. If the recovery standard area is outside the upper or lower limits, flag all related positive and non-detect data (EMPC/EDL) with "J" regardless whether the internal standard recoveries met specifications or not.

2. If extremely low area counts (<25%) are reported, reject all associated non-detect data (R) and flag the positive data (J).

3. If the retention time of the recovery standard differs by more than 10 seconds from the daily calibration use professional judgement to determine the effect on the results. A time shift of more than 10 seconds may cause certain analytes to elute outside the retention time window established by the GC column performance check solution.

5.1 List samples qualified due to recovery standard excursions.

Instrument:

Sample ID (client/lab ID)	**Recovery Standard**	**Area and Percent Recovery**	**Action**

6.0 MATRIX SPIKE

Note: For air samples, MS/MSD samples may not be collected since duplication of air samples (collected for spiking with target compounds) may be difficult to achieve. Consult Project Manager.

Criteria:
The results obtained from the MS and MSD samples (concentrations of 2,3,7,8-substituted PCDDs/PCDFs) should agree within 20 percent relative difference.

.1 Was a matrix spike analyzed at the frequency of one per SDG samples per matrix?

.2 Was the percent recovery of 2378-TCDD and other 2378-substituted PCDDs/PCDFs within 50 to 150 percent?

VALIDATION ACTIONS:
If problems such as interferences are observed, use professional judgement to assess the quality of the data. The 50-150% limits of the matrix spike data may be used to flag data of the spiked sample only.

6.1 List samples qualified due to matrix spike excursions.

INSTRUMENT:

Matrix Spike ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

7.0 DUPLICATE SAMPLES

Criteria:

The results of the laboratory duplicates (percent recovery and concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree within 25 percent relative difference (difference expressed as percentage of the mean).

For every batch of 20 samples or samples collected over a period of one week, whichever is less, there must be a sample designated as duplicate. Were duplicate samples collected at the above frequency?

Did results of the duplicate samples agree within 25% relative difference for 2,3,7,8 substituted isomers and 50% for the rest of the congeners?

VALIDATION ACTION:

The duplicate results must be used in conjunction of other QC data. If no hits are reported, precision may be assessed from the internal standard recoveries.

7.1 List samples qualified due to duplicate excursions.

INSTRUMENT:

Duplicate ID	Analyte	Excursion	Samples Affected (client/lab ID)	Action

8.0 FIELD DUPLICATE ANALYSIS

For Region V, field duplicates are only listed in the validation report and RPDs calculated. Samples are not evaluated based on field duplicate results.

8.1 Were field duplicates collected and analyzed at the frequency specified in the site specific QAPP?

Summarize below compounds that did not meet above criteria.

Duplicate IDs	Compound	RPD	Actions	Samples Affected

Addendum to work plan

Objectives:

Additional sediment data will be collected in the vicinity of the coal tar impacted area of the river to further define the extent of total PAH concentrations greater than 4 ppm. The data will be of sufficient quality to support uses for risk assessment, feasibility study, or remedial action at the site.

Procedures:

Locations:

Sediment will be collected at locations identified in Table 1. It is assumed that prior to sampling, NYSEG personnel will reestablish shoreline transect locations by field survey.

Collection Procedures:

Consistent with previous sampling (OBG 1998), prior to sampling for a location the area will be probed with a steel rod or pipe. The rod or pipe will be examined for visual evidence or odors of coal tar. If evidence of coal tar is observed, it will be noted in field logs and the location will be assumed to contain PAH concentrations exceeding the 4 ppm total PAH screening level. Therefore, sampling of such a location will not be required and an alternative location will be selected for sampling. Similarly, if a sediment sample is collected that exhibits either visual evidence of odors of coal tar, the result will be documented in the field notes and the sample will be retained for disposal in the laboratory. Analysis of such a sample will not be required.

Sediment sampling will be performed using manual push core methods. The push core sampling device will be adapted for use with an auger head. This technique was found to be more successful than conventional push cores for penetrating sediment and cobble material typical of the subject region of the Susquehanna River. The auger head push core sampling device will be constructed to allow sediment up to 2 to 3 feet in depth. Past sampling using manual methods at these depths has been problematic. It is hoped that the sampling device will overcome these difficulties.

The sampling device will consist of a stainless steel core tube with an interior tube of lexan. A core-catcher may be used to help retain sediment in the tube. Upon collection the core will be extruded and samples will be collected at 6" intervals from the interior of the core and placed in jars. It must be recognized that while the auger device facilitates collection of sediment samples from a rock & cobble type river bed, it also may disturb sediment layering and contact of interior sediment to the wall of the sampler may be possible. This would potentially affect the representativeness of lower samples, if contact with residuals on the sampling device occurred during sample retrieval.

Analyses:

Sediment samples will be analyzed for PAHs by method USEPA 8270C and total organic carbon (TOC) by the Lloyd Kahn method. Three samples will be analyzed for grain size. Samples will be archived in the laboratory. Data will be provided in a data validatable package, New York State Analytical Services Program (ASP) Category B deliverables. However, the data will not be validated at this time.

Data evaluation:

Delineation of the coal tar impacted area will be based on computation of confidence intervals to demonstrate that the area is defined within the total PAH criteria of 4 ppm. Confidence intervals will be established using the t-test. Average concentration less than the total PAH concentration of 4 ppm based on data from at least 3 samples. Individual concentrations should not exceed the target criteria by more than 100%.

Reference: Gilbert

Data will be evaluated according to New York State sediment screening guidance.

Health and Safety:

The site-specific health and safety plan prepared by Blasland, Bouck, & Lee (1997) and the addendum prepared by O'Brien & Gere Engineers, Inc. (1998) will apply to the sediment sampling program described above.

Quality Assurance:

The site-specific Quality Assurance Project Plan by Blasland, Bouck, & Lee (1997) and the addendum prepared by O'Brien & Gere Engineers, Inc. (1998) will apply to the sediment sampling program described above.

Table 1. Sample locations and rationale for collection

Purpose	*Quantity*	*Description*
Background	4	Samples will be collected upstream of SD1 to evaluate sediment concentrations closer to the site. Previous sampling in that area was not successful due to difficulties applying push core techniques to that area. It is hoped that push/auger type sampling proposed in this addendum will overcome some of those difficulties. Three samples will be collected perpendicular to the north shore to represent surface samples at near shore, 20 feet and 40 feet from shore. An additional background sample will be collected along the south shore to represent upstream concentrations that may occur in that area.
Upstream boundary of coal tar impacted area	3	Samples collected at SD8-In, 20 and 40
Midstream	7	Samples collected at 25ft intervals, approximately 60 ft from shore along stations positioned parallel to shore. Samples will be collected at SD8-60, SD8.25-60, SD9-60, SD9.25-60, SD10-60, SD10.25-60 and SD11-60.
Downstream	3	Samples will be collected at SD11-IN, SD11-25, and SD11-50.
Depth samples collected within the coal tar impacted area	3	The intent of the depth samples is to define the vertical extent of contamination within the coal tar impacted area. Three depth samples will be collected to a depth of 3 feet if possible, samples collected at the 1.0-1.5 ft interval will be analyzed. The remaining samples will be archived. Lower depth samples may be analyzed if total PAHs are present in the 1.0-1.5 ft interval.
Replicate samples	2	collected in the vicinity of SD9-70 and SD8.15-20 to evaluate the representativeness of data collected at these locations in 1999.
Quality Assurance	5	Samples will consist of a matrix spike and matrix spike duplicate pair, and a blind field duplicate collected at a frequency of 1/20 environmental samples. An equipment rinse blank will be collected at a frequency of 1/20 environmental samples or 1/day, which ever is less.
Additional	14	Based on the results of the sampling outlined above, additional samples may be necessary to complete the characterization of the coal tar impacted area. Quantity presented assumes 10 environmental samples and 4 QA/QC samples will be required.
Total	33	